



# Geochemistry, Geophysics, Geosystems

## RESEARCH ARTICLE

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### Special Section:

Magmatic and volcanic processes in continental rifts

### Key Points:

- Alkali feldspars have variable trace element (Ba) concentrations, some far from equilibrium with their carrier liquids (melts)
- Some feldspars are *antecrysts* (in equilibrium with a liquid on the line of descent, but not the host melt), picked up from a crystal mush
- Ignimbrites erupted during caldera-forming events are dominated by antecrysts, perhaps scavenged from deep parts of the magma reservoir

### Supporting Information:

- Supporting Information S1
- Data Set S1

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## Mixing and Crystal Scavenging in the Main Ethiopian Rift Revealed by Trace Element Systematics in Feldspars and Glasses

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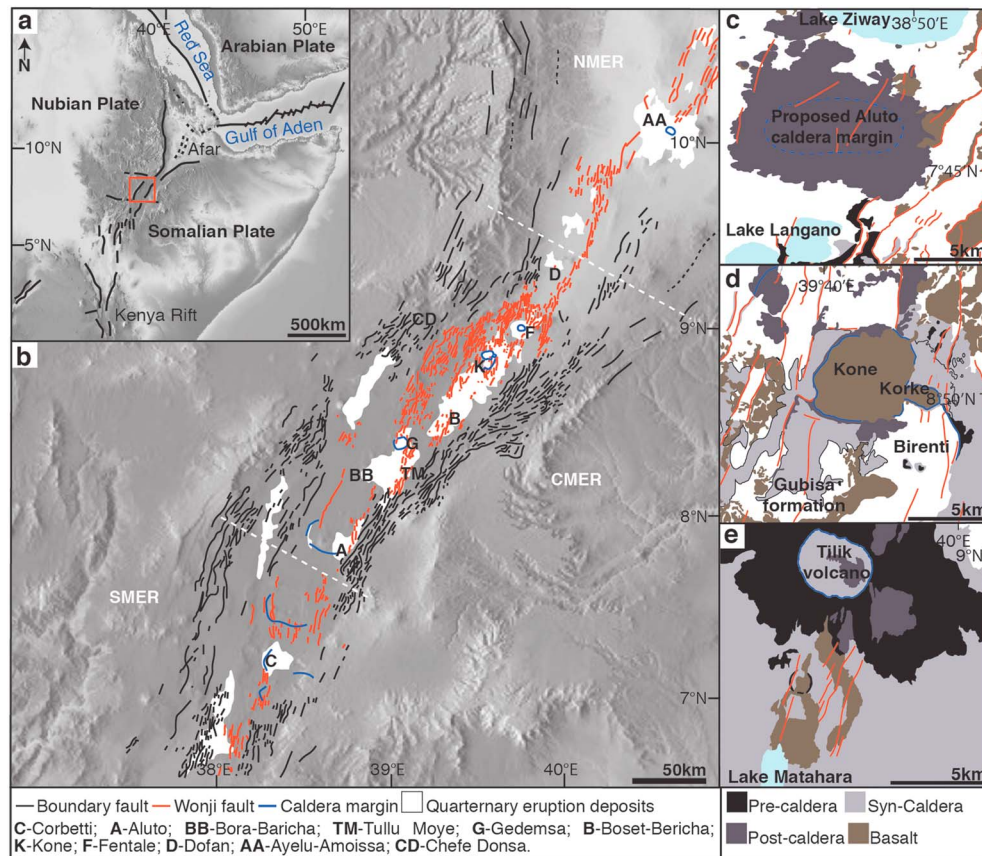
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**Abstract** For many magmatic systems, crystal compositions preserve a complex and protracted history, which may be largely decoupled from their carrier melts. The crystal cargo may hold clues to the physical distribution of melt and crystals in a magma reservoir and how magmas are assembled prior to eruptions. Here we present a geochemical study of a suite of samples from three peralkaline volcanoes in the Main Ethiopian Rift. While whole-rock data show strong fractional crystallization signatures, the trace element systematics of feldspars, and their relationship to their host glasses, reveals complexity. Alkali feldspars, particularly those erupted during caldera-forming episodes, have variable Ba concentrations, extending to high values that are not in equilibrium with the carrier liquids. Some of the feldspars are antecrysts, which we suggest are scavenged from a crystal-rich mush. The antecrysts crystallized from a Ba-enriched (more primitive) melt, before later entrainment into a Ba-depleted residual liquid. Crystal-melt segregation can occur on fast timescales in these magma reservoirs, owing to the low-viscosity nature of peralkaline liquids. The separation of enough residual melt to feed a crystal-poor postcaldera rhyolitic eruption may take as little as months to tens of years (much shorter than typical repose periods of 300–400 years). Our observations are consistent with these magmatic systems spending significant portions of their life cycle dominated by crystalline mushes containing ephemeral, small (< 1 km<sup>3</sup>) segregations of melt. This interpretation helps to reconcile observations of high crustal electrical resistivity beneath Aluto, despite seismicity and ground deformation consistent with a magma body.

## 1. Introduction

Studies of magma storage and migration in the crust over the past decade have challenged traditionally held views of magma chambers as large, molten melt bodies (see reviews by Cashman & Giordano, 2014; Cashman & Sparks, 2013; Cashman et al., 2017). High-precision, high-resolution geochemical studies of erupted volcanic products have revealed previously undetected complexities at the mineral scale. Many systems show evidence of magmas being stored, between eruptions, at near-solidus conditions for prolonged periods of time (e.g., Bachmann & Bergantz, 2008; Cashman et al., 2017; Cooper & Kent, 2014). Heterogeneous crystal cargoes in volcanic rocks, which are often not in equilibrium with their carrier liquids, suggest that mixing may be ubiquitous. Crystal-rich mushes may be disrupted and disaggregated prior to and during eruptions, leading to the accumulation of a range of diverse crystals in the magma, for example, Fish Canyon Tuff (Bachmann et al., 2002), Shiveluch Volcano (Humphreys et al., 2008), Mount Hood (Cooper & Kent, 2014), and Yellowstone (Wotzlaw et al., 2014). Added to these geochemical lines of evidence, geophysical imaging of the upper crust has often failed to detect large bodies of melt beneath active volcanoes (e.g., Hübert et al., 2018; Manzella et al., 2004; Samrock et al., 2015). This has led to suggestions that, in some circumstances, magmas may be stored as melt-poor mush, which is expected to have a low electrical conductivity and low  $V_p/V_s$  ratio (Chu et al., 2010; Miller & Smith, 1999; Steck et al., 1998; Zandt et al., 2003).

Many studies are published on the crystal cargoes of large magma reservoirs in metaluminous, calc-alkaline magmatic systems; to date, there has been little attention paid to the crystal cargoes of peralkaline magma reservoirs, despite their prevalence in continental rift settings. There are few constraints on the architecture and dynamics of peralkaline magma reservoirs, and little is known about the types of geophysical signals



**Figure 1.** (a) Map locating the Main Ethiopian Rift (b) within the larger eastern branch of the East African Rift system. Peralkaline calderas are outlined in dark blue, with Quaternary eruption deposits highlighted in white (Corti, 2008). The red lines represent the Wonji Fault Belt, where the majority of extensional stress is accommodated; the black lines represent the older, less active border faults (Corti, 2008). Aluto volcano is located at the southern end of the central Main Ethiopian Rift, Kone and Fentale are located at the northern end; simplified geological maps (adapted from Hutchison, Pyle, et al., 2016; Rampey et al., 2010; Gibson, 1974) are shown for both (c–e, respectively).

such magma bodies would generate. Peralkalinity, defined as having an excess of alkalis with respect to aluminium (molar  $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 > 1$ ; Shand, 1927), has a strong influence on melt rheology, and thus magma behavior (Lanzo et al., 2013; Neave et al., 2012; Stevenson & Wilson, 1997). The elevated alkali content of peralkaline melts, coupled with high dissolved halogen contents (Barclay et al., 1996), results in peralkaline liquids having much lower viscosity (by 2 to 3 log units) compared to their metaluminous counterparts, particularly at temperatures approaching the solidus (di Genova et al., 2013). The low viscosity of peralkaline melts likely influences magma reservoir processes. Crystal-melt segregation via settling and/or compaction within the crustal storage system may occur faster than in metaluminous arc settings for similar melt  $\text{SiO}_2$  contents (Macdonald, 2012; Neave et al., 2012), and magma reservoirs may become more rapidly density-stratified, hindering overturn and mixing (Blake & Ivey, 1986; Macdonald, 2012; Mahood & Hildreth, 1986; Neave et al., 2012; Peccerillo et al., 2003).

The Main Ethiopian Rift (MER) is a northerly segment of the East African Rift system (EARS; Figure 1a), a present-day example of continental rifting. Whole-rock compositions of rift magmas are commonly bimodal (Boccaletti et al., 1995; Gasparon et al., 1993; Hutchison, Pyle, et al., 2016; Macdonald et al., 2011; Mazzarini et al., 2004; Peccerillo et al., 2003; Ronga et al., 2010; Rooney, Hart, et al., 2012; Trua et al., 1999). Alkali basalts erupt outside the calderas and along faults (Mazzarini et al., 2013; Rooney et al., 2011), while peralkaline trachytes and rhyolites dominate the eruptive products from axis-central volcanoes. Isotope and trace element systematics of whole-rock material indicate the rhyolites are derived from protracted fractional crystallization of an alkali basalt parent (Giordano et al., 2014; Hutchison et al., 2018; Hutchison, Pyle, et al., 2016; Macdonald et al., 2011; Peccerillo et al., 2003). Modeling suggests that the least evolved trachytes at Gedemsa Volcano

(location shown in Figure 1b) are generated after ~70% fractional crystallization of the basalts, and peralkaline rhyolite after an additional ~20% (Peccerillo et al., 2003). The transition to peralkalinity in these magmas occurs after 80% to 85% crystallization, when the dominant crystallizing phase changes from sodic plagioclase to alkali feldspar (Bailey & Schairer, 1964; Barberi et al., 1974), causing the melt to evolve towards the minimum in the  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system (Carmichael & MacKenzie, 1963).

Despite seemingly simple whole-rock geochemical signatures, controlled by fractional crystallization, there is petrological and geochemical evidence for more complex magma processing prior to eruptions at MER volcanic centers. For example, heterogeneous glass compositions, zoned feldspar and clinopyroxene phenocrysts, and resorbed feldspar and olivine phenocrysts have been cited as evidence for magma mixing at Boset-Bericha volcano (Macdonald et al., 2011), while mingled glass compositions have been observed at Chefe Donsa (Rooney, Hart, et al., 2012) and intermediate-composition enclaves have been found in erupted products from Aluto (Hutchison, Pyle, et al., 2016) (locations shown in Figure 1b). High Ba and Mn concentrations in porphyritic trachytes from Gedemsa volcano (location shown in Figure 1b) have been linked to feldspar and fayalite accumulation, with mass balance calculations suggesting a minimum of 10% crystal accumulation (Peccerillo et al., 2003). The resorbed nature of some phenocrysts is consistent with an antecrystic nature (Peccerillo et al., 2003). The petrology of these complex erupted products may encode information about how magmas are stored and remobilised during eruptions, which may be relevant to interpreting geophysical data acquired in the region. Significant portions of melt may be held in crystal-rich magma reservoirs, ready to be remobilised and extracted (e.g., Bachmann & Bergantz, 2008; de Silva et al., 2008; Ruprecht & Bachmann, 2010; Wark et al., 2007), but these melt regions can be difficult to detect using geophysical techniques. For example, there is debate concerning the current state of the magma reservoir beneath Aluto volcano. Seismic and deformation data, combined with geobarometric estimates and Holocene eruptive frequency (Fontijn et al., 2018; Hutchison, Biggs, et al., 2016; Hutchison, Pyle, et al., 2016; Wilks et al., 2017), point to the existence of a shallow magma storage system. However, magnetotelluric methods fail to identify a volume of enhanced electrical conductivity in the crust (Hübert et al., 2018; Samrock et al., 2015) that might indicate the presence of partial melt (e.g., Pous et al., 1999; Hoffman-Rothe et al., 2001; Schilling & Partzsch, 2001). In contrast, enhanced electrical conductivity, interpreted as the presence of crustal melt, has been imaged in similar surveys at the nearby Boset-Bericha volcano (Whaler & Hautot, 2006).

We hypothesize that melt-poor mush may dominate magma reservoir storage systems beneath central volcanoes in the MER and that this mush may be efficiently constructed in peralkaline magmatic systems due to their unique rheological characteristics. To test this hypothesis we undertake a systematic comparison between whole-rock, glass and feldspar compositions for a suite of samples from three peralkaline MER volcanoes, Aluto, Kone, and Fentale (locations shown in Figure 1b). We focus on Ba, as it partitions strongly into alkali feldspars, the overwhelmingly dominant crystallizing phase in evolved peralkaline magmas; and on Zr, a highly incompatible element in peralkaline melts and a useful proxy for fractional crystallization. We evaluate the extent to which the crystal cargo is in equilibrium with its carrier liquid by comparing the results from the natural samples with experimental partitioning data for Ba using models of fractional crystallization generated from RhyoliteMELTS (Gualda et al., 2012). Models of crystal settling and compaction (Bachmann & Bergantz, 2004) are used to assess the degree of influence of peralkaline liquid rheology on timescales of crystal-melt segregation processes. Finally, inferences about the types of geophysical signals such magma bodies would generate are made, helping to inform future volcanic monitoring activities along the MER.

## 2. Geological Setting

The MER is part of the EARS (Figure 1a), a continental rift between the Nubian and Somalian plates (see reviews by Corti, 2009; Ebinger, 2005). Extending in a NNE-SSW direction from the Afar to the Turkana depression (Mohr, 1983; WoldeGabriel et al., 1990), the MER is currently undergoing active east-west extension of ~5 mm/year (Saria et al., 2014). Extension was initially accommodated by displacement along NE-SW trending faults (Bonini et al., 2005; WoldeGabriel et al., 1990). Since 2 Ma, strain has largely been accommodated on the Wonji Fault Belt (WFB) (Corti, 2009) and recent geodetic data confirms that 80% of the current strain is taken up here (Bilham et al., 1999). The WFB is a group of short N-NE trending en echelon faults that lie within a ~15-km-wide axial zone in the MER (Agostini et al., 2011; Keir et al., 2015, 2006). Pleistocene and Holocene

volcanism has been focused within tectono-magmatic segments along the rift that are colocated with the WFB (Abebe et al., 2007; Corti, 2009; Fontijn et al., 2018; Keir et al., 2015, 2006; Rooney et al., 2011).

Aluto, Kone, and Fentale are peralkaline caldera complexes located in the MER (Figures 1b and 1c, 1d, and 1e, respectively). Whole-rock compositions, petrographic descriptions and geochronology for Aluto volcanic products are presented by Hutchison, Pyle, et al. (2016), and for Fentale by Gibson (1974) and Giordano et al. (2014). In contrast, there are few data available for Kone volcano. Cole (1969) and Rampey et al. (2010) provide descriptions of major map units; however, previous petrographic and geochemical investigations have largely been limited to a Plinian eruptive deposit known as the Gubisa formation (Figure 1d; Rampey et al., 2014), with some limited data also available on basalts that infill the caldera structure (Furman, 2007; Rooney et al., 2007; Rooney, Hanan, 2012).

The Kone central volcanic complex comprises the older  $\sim 95$  km<sup>2</sup> caldera (Birenti), and the younger, 22 km<sup>2</sup> Kone caldera with a small embayment of 2 km<sup>2</sup> known as the Korke caldera (Rampey et al., 2010, 2014; Figure 1d). Both structures are thought to have formed during a multieruption event, with the later Kone and Korke calderas developing during a series of three to four sub-Plinian and Plinian eruptions (Rampey et al., 2010, 2014). The Gubisa formation is associated with the formation of the Kone caldera (Figure 1d); deposits are up to 60 m thick with a minimum volume of 3.2 km<sup>3</sup> (Rampey et al., 2014). Deposits associated with caldera-forming events are well preserved and dominate surface exposure at the Kone volcanic complex. Trachytic and rhyolitic lava domes and associated minor deposits of pumice preceded and followed the caldera-forming events. There are no dates available for Kone eruptions, though tectonically controlled basaltic lava effusion, exploiting the join between the Kone and Korke calderas and filling both structures (Figure 1d), likely represents the most recent volcanism (Fontijn et al., 2018; Rampey et al., 2010, 2014). Basaltic scoria cones and fissure lavas are also present to the Southwest and Northeast (Figure 1d), aligned with the WFB (Rampey et al., 2010, 2014).

Fentale volcano is the northernmost silicic center in the MER, located at the junction with the Afar region (Figure 1b; Gibson, 1967, 1969, 1970, 1974). It is a 600 m high stratocone built of silicic lava flows and rare tephra horizons, with a 300 m deep summit caldera known as Tilik volcano (Figure 1e; Gibson, 1967, 1969, 1970, 1974; Giordano et al., 2014; Kidane et al., 2009; Webster et al., 1993). The 30 km<sup>2</sup> caldera is roughly elliptical in shape and is thought to have formed during an explosive eruption between 0.17 and 0.151 Ma (Williams et al., 2004). The deposits of this eruption are widespread, forming intensely welded tuffs up to 30 m thick, blanketing the plain and covering the slopes of the earlier edifice (Figure 1e; Giordano et al., 2014). Postcaldera volcanism consists largely of obsidian lava flows from vents within the caldera itself and on the volcano's flanks, as well as from fissures along the rim (Acocella et al., 2002; Fontijn et al., 2018; Gibson, 1967, 1969, 1970, 1974; Webster et al., 1993; Williams et al., 2004). Minor postcaldera explosive episodes have also occurred, with scattered pumice observed on the edifice slopes (Fontijn et al., 2018) and a significant pumice cone on the southern flank. Similar to Kone; the most recent activity was mafic, primarily on the southwestern side of the volcano, where the WFB intersects the Fentale complex. Here fissure lavas cover a 3 km<sup>2</sup> area (Figure 1e) and have been dated to  $\sim 1810$ – $1820$  based on oral tradition (Harris, 1844).

At Aluto volcano at least 8–21 km<sup>3</sup> of welded, green rhyolitic ignimbrites and trachytic tuffs erupted during the formation of a 42 km<sup>2</sup> caldera structure at ca. 300 ka. It is not possible to identify if this was a single or multiple-eruption event, due to the generally poor surface exposure of these deposits (Hutchison et al., 2015; Hutchison, Pyle, et al., 2016). Postcaldera volcanism has been ongoing since at least ca. 60 ka, possibly after a significant hiatus (Hutchison, Pyle, et al., 2016), and dominates the exposed volcanic rocks (Figure 1c). These postcaldera eruptions are thought to typically initiate with explosive eruptions, building small pumice cones and/or emplacing pyroclastic density currents, before effusive eruptions of obsidian coulées (Hutchison, Pyle, et al., 2016). Basaltic volcanism is largely confined to scoria cones and fissure lavas to the northeast of the main edifice (Figure 1c). Hutchison, Pyle, et al. (2016) suggest a relationship between the basalts and the caldera system based on proximity and comparable surface weathering of eruptive products, though the cones are strongly aligned with the WFB. It is hypothesized that silicic magma chambers in the MER act as mechanical density filters, forcing mafic melts to erupt externally to caldera margins (Peccerillo et al., 2003). The most recent dated eruption occurred several hundred years ago ( $0.4 \pm 0.05$  cal ka BP; Hutchison, Pyle, et al., 2016), and at least 25 eruptions are identified in the Holocene period (Fontijn et al., 2018).



Episodes of ground deformation, thought to have a magmatic origin, have occurred at Aluto volcano over at least the past decade (Biggs et al., 2011; Hutchison, Biggs, et al., 2016). Interferometric synthetic aperture radar (InSAR) observations show periods of rapid inflation followed by periods of long-term subsidence. The inflation is thought to reflect fluid injection into the roof zone of a magma storage region, while subsidence was interpreted as magmatic degassing and depressurization of the hydrothermal system (Hutchison, Biggs, et al., 2016). The deformation is consistent with a source at ~5 km depth. Seismicity has been identified between 2- and 9-km depth, which also reflects magmatic fluids causing elastic deformation (Wilks et al., 2017). However, magnetotelluric methods fail to identify a volume of enhanced electrical conductivity at this depth in the crust (Hübert et al., 2018; Samrock et al., 2015) that might indicate the presence of partial melt (e.g., Pous et al., 1999; Hoffman-Rothe et al., 2001; Schilling & Partzsch, 2001).

### 3. Analytical Techniques

The Aluto samples used in this study were collected by William Hutchison between 2012 and 2014. The Kone samples were collected by Michael Rampey between 2001 and 2003 and Karen Fontijn and Keri McNamara in November 2015. The Fentale samples were collected by Fiona Iddon, Jonathan Hunt, and Abate Assen in October 2017. Caldera-forming ignimbrites, postcaldera silicic lava and pumice, and later postcaldera basaltic lava and scoria were collected at each site. Where available precaldra silicic lava and pumice and pumice associated with caldera-forming episodes was also utilized in the study. See Tables 1 and 2 for all sample locations and refer to Hutchison, Pyle, et al. (2016) for full details on the Aluto samples.

Kone and Fentale samples were trimmed to access clean regions and then crushed and milled to produce powders. X-ray fluorescence spectrometry analysis was used to acquire whole-rock major and trace element compositional data on fusion beads and powder pellets respectively. Loss on ignition was determined at 950 °C. Data were acquired at the Department of Geology at the University of Leicester using a PANalytical Axios-Advanced X-ray fluorescence spectrometry spectrometer. Precision of 5% for majors (11% for MnO, 8% for P<sub>2</sub>O<sub>5</sub>) and 6% for trace elements was achieved using a range of secondary standards; Ba showed a precision of 4% and Zr a precision of 1%. An accuracy of 7% (11% for P<sub>2</sub>O<sub>5</sub>) was achieved for majors and 10% for trace elements; Ba was analyzed with an accuracy of 9% and Zr an accuracy of 6%. Standards compilations can be found in the supporting information. Precision and accuracy (in %) were calculated as  $100 \frac{\sigma}{\bar{x}}$

and  $100 \frac{(\bar{x} - x_{\text{ref}})}{x_{\text{ref}}}$  respectively.

Polished sections (30–50 μm thick) were used for petrographic analysis and geochemical analyses of phenocryst phases. The Quanta-650F scanning electron microscope at the Department of Earth Sciences of the University of Cambridge was used to acquire backscattered electron images and maps to assess sample crystal fraction and to provide microtextural information. A 15-kV beam and 4-μm spot was used for Aluto samples; a 10-kV beam and 5-μm spot was used for Kone samples (images were acquired by different operators). QEMSCAN software was used for quantitative analysis, and to assess the major phases present and major element zoning. The QEMSCAN software creates phase assemblage maps from data acquired from a combination of low-count energy-dispersive X-ray spectra and backscattered electron brightness and X-ray count information. Fiji software, an open source image processing package (Schindelin et al., 2012), was used to quantitatively assess crystal fraction.

Chemical compositions of the main phases and the matrix glass were measured using a Cameca SX-100 Electron Probe Micro-Analyzer at the University of Cambridge. An accelerating voltage of 15 kV was used for all analysis. A defocused beam of 10 μm and a current of 10 nA was used for glass analyses. A precision and accuracy of 6% for major elements (precision of 10% for MnO and 9% for P<sub>2</sub>O<sub>5</sub>; accuracy of 8% for MnO and 41% for P<sub>2</sub>O<sub>5</sub>) was achieved using a range of secondary standards. Plagioclase and alkali feldspar were also measured using a 10 nA beam but with a defocused beam of 5 μm. Pyroxenes were measured using a 1 μm sized beam with a current of 10 nA. For all phases some trace elements were measured using a second condition with a higher current voltage of between 40 and 100 nA. Counting times of 10–30 s were used for major elements, 40–90 s for trace elements and 10–12 s for alkalis. Where the beam current was increased to 100 nA, for example for the measurement of Ba and Sr within feldspars, counting times of up to 400 s were used. A precision of 6% and an accuracy of 3% for major elements (precision of 31% for TiO<sub>2</sub> and

**Table 1**  
Selected Whole-Rock Data for Kone and Fentale Volcanoes Acquired via XRF Analysis at the Department of Geology at the University of Leicester

		Sample															
Rock type		Kone3.9	Kone3.18	Kone3.30	Kone3.41	Kone4.10	K04	K05	K06	K07	KoneBG25	KoneBN29	MER128A	MER130A	MER133A		
		Pumice airfall	Pumice airfall	Porphyritic obsidian	Pumice airfall	Porphyritic obsidian	Porphyritic obsidian	Ignimbrite	Pumice lapilli	Porphyritic obsidian	Porphyritic obsidian	Welded ignimbrite	Pumice lapilli breccia	Pumice lapilli breccia	Basalt scoria		
Relative age		Kone	Kone	Post-Kone	Kone	Pre-Kone	Pre-Birenti	Birenti	Post-Kone	Post-Kone	Pre-Kone	Kone	Kone	Kone	Post-Kone caldera		
		caldera	caldera	caldera	caldera	caldera	caldera	caldera	caldera	caldera	caldera	caldera	caldera	caldera	Post-Kone caldera		
Location	Lat. (N)	8.8178	8.8280	8.8691	8.8244	8.8628	8.7875	8.7875	8.8156	8.8158	Northwest	South wall	8.7877	8.8091	8.8544		
	Long. (E)	39.6769	39.6538	39.7250	39.6591	39.6640	39.7383	39.7383	39.6995	39.7008	rim of Kone	Kone	39.6589	39.6873	39.7469		
	wt%	66.20	66.73	70.01	72.01	70.15	70.14	70.28	72.69	71.64	70.73	66.71	65.24	69.36	46.40		
	wt%	0.40	0.29	0.46	0.23	0.39	0.46	0.48	0.21	0.23	0.39	0.47	0.51	0.23	1.99		
	wt%	10.90	7.45	9.30	10.27	7.93	9.32	10.18	8.11	8.42	7.89	11.39	8.95	8.40	15.14		
	wt%	6.56	8.52	8.34	4.54	9.16	7.92	8.27	8.57	7.97	8.98	7.00	7.67	6.28	12.04		
	wt%	0.24	0.29	0.28	0.14	0.30	0.30	0.30	0.31	0.29	0.33	0.30	0.30	0.23	0.18		
	wt%	0.06	0.08	0.03	0.08	0.04	0.02	0.11	0.07	0.07	0.04	0.09	0.28	0.16	8.42		
	wt%	0.45	0.38	0.38	0.28	0.38	0.41	0.88	0.60	0.34	0.36	0.59	1.80	0.62	10.15		
	wt%	4.57	6.43	6.39	4.63	6.67	6.49	5.64	3.12	6.76	6.68	6.05	3.63	3.90	2.84		
	wt%	4.95	4.69	4.40	4.94	4.32	4.37	4.08	5.65	4.16	4.29	4.64	5.09	5.52	0.85		
	wt%	0.03	0.03	0.03	0.02	0.03	0.02	0.03	0.02	0.02	0.02	0.04	0.03	0.02	0.51		
	wt%	3.44	3.48	-0.27	2.26	-0.36	-0.01	0.06	0.24	-0.01	-0.34	2.18	5.44	4.28	0.25		
Total	wt%	99.17	98.38	98.85	99.40	99.03	99.45	100.29	99.59	99.90	99.39	99.48	98.98	99.02	98.77		
Al <sub>2</sub>	ppm	1.18	2.10	1.64	1.26	1.97	1.65	1.35	1.39	1.86	1.98	1.32	1.28	1.47	0.37		
Ba	ppm	176.7	95.6	53.1	39.2	79.0	64.6	146.7	248.8	220.6	83.6	591.6	65.5	30.4	395.5		
Ce	ppm	214.3	275.7	206.8	203.4	295.7	220.9	246.0	334.7	274.6	329.0	192.1	208.0	471.1	52.0		
Co	ppm	2.4	3.7	5.2	1.5	4.3	3.6	1.5	3.4	2.6	4.7	5.0	4.8	5.0	51.7		
Cr	ppm	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	326.1		
La	ppm	102.2	120.9	100.9	97.1	139.7	110.5	125.2	166.5	135.4	153.8	92.9	99.0	227.6	22.6		
Nb	ppm	156.0	209.7	143.0	132.6	223.6	145.1	158.2	215.0	179.3	228.5	125.7	127.6	325.8	29.6		
Ni	ppm	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.1	5.6	121.1		
Rb	ppm	124.6	162.2	142.7	178.6	168.5	145.4	132.9	220.1	161.2	173.6	102.7	131.1	332.2	14.7		
Sr	ppm	5.3	11.5	3.8	10.0	6.4	bdl	23.8	37.9	6.1	6.0	10.8	81.0	27.4	427.1		
Th	ppm	16.9	21.1	18.2	20.2	23.5	18.0	18.3	25.7	20.7	23.6	13.6	14.8	45.3	1.9		
Y	ppm	118.9	170.1	117.5	99.1	175.4	120.1	84.4	188.1	152.5	179.6	100.9	110.5	243.3	30.4		
Zr	ppm	1029.7	1324.6	947.0	882.1	1411.6	1006.2	1077.4	1486.2	1215.9	1447.9	832.9	836.8	2141.9	152.0		

Note. LOI = loss on ignition; bdl = below detection limit (all values reported are above detection limits); Al<sub>2</sub> = algaipitic index (molar (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub>); XRF = X-ray fluorescence spectrometry.

Note. LOI = loss on ignition; bdl = below detection limit (all values reported are above detection limits); A.I. = agpaite index (molar (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub>); XRF = X-ray fluorescence spectrometry.

**Table 1** (continued)

		Sample														
Rock type		MER136A	MER137A	MER138A	MER140Bb	F01	F03	F12	F16	F27	F41	F44	F48	F49		
		Basalt scoria	Basalt scoria	Basalt scoria	Welded ignimbrite	Porphyritic obsidian	Pumice lapilli	Basaltic scoria	Porphyritic obsidian	Porphyritic obsidian	Pumice lapilli	Welded ignimbrite	Welded ignimbrite	Basalt scoria		
Relative age		Post-Kone caldera	Post-Kone caldera	Post-Kone caldera	Kone caldera	Precaldera	Precaldera	Postcaldera	Postcaldera	Precaldera	Post-caldera	Caldera	Caldera	Postcaldera		
Location	Lat. (N)	8.8239	8.8292	8.8418	8.8434	8.9978	8.9978	8.9381	8.9584	8.9776	8.9578	8.9577	8.9279	8.9525		
	Long. (E)	39.7047	39.7096	39.7139	39.7332	39.8709	39.8709	39.8927	39.9271	39.8733	39.8992	39.8986	39.8432	39.7550		
SiO <sub>2</sub>	wt%	46.48	46.32	46.25	72.07	69.56	70.11	46.94	71.65	69.63	71.76	69.24	69.98	46.45		
TiO <sub>2</sub>	wt%	2.23	2.17	2.29	0.37	0.52	0.50	3.92	0.38	0.48	0.35	0.51	0.42	2.44		
Al <sub>2</sub> O <sub>3</sub>	wt%	14.65	14.54	14.71	10.09	9.59	9.32	13.62	9.41	8.23	8.99	9.83	9.15	15.58		
FeO <sub>T</sub>	wt%	12.60	12.54	12.60	6.34	8.42	8.36	15.51	7.40	9.40	7.45	8.65	8.47	13.03		
MnO	wt%	0.19	0.19	0.19	0.22	0.36	0.33	0.28	0.28	0.40	0.28	0.33	0.33	0.18		
MgO	wt%	8.81	9.23	8.58	0.10	0.02	0.07	4.78	0.20	0.05	0.06	0.18	0.11	8.26		
CaO	wt%	10.55	10.51	10.68	0.37	0.47	0.86	9.04	0.81	0.41	0.41	0.72	0.54	10.44		
Na <sub>2</sub> O	wt%	3.10	2.93	3.09	5.49	6.82	5.44	3.96	6.29	6.83	5.83	6.50	6.40	2.95		
K <sub>2</sub> O	wt%	0.97	0.92	0.99	4.43	4.13	4.54	0.89	3.80	4.19	4.21	3.99	4.26	0.73		
P <sub>2</sub> O <sub>5</sub>	wt%	0.52	0.48	0.55	0.03	0.03	0.03	1.18	0.07	0.03	0.02	0.05	0.03	0.45		
LOI	wt%	−0.55	−0.36	−0.32	0.18	−0.02	0.18	−0.03	−0.01	−0.02	0.13	0.07	0.13	0.50		
Total	wt%	99.58	99.50	99.61	99.67	99.91	99.75	100.20	100.28	99.69	99.55	100.07	99.86	101.01		
Al <sub>2</sub>		0.42	0.40	0.42	1.37	1.64	1.49	0.55	1.54	1.92	1.57	1.53	1.65	0.36		
Ba	ppm	391.3	364.6	425.7	208.6	637.2	702.0	474.2	269.2	769.9	422.5	614.0	530.2	274.6		
Ce	ppm	62.8	59.0	63.4	275.9	240.6	259.7	68.2	319.5	266.1	320.8	239.7	255.7	46.3		
Co	ppm	51.5	52.9	48.9	4.2	3.8	2.0	27.2	3.3	3.0	4.2	2.1	2.9	48.1		
Cr	ppm	386.1	435.7	351.5	bdl	bdl	bdl	6.7	bdl	bdl	6.7	bdl	bdl	219.5		
La	ppm	32.1	24.7	31.0	127.5	119.3	130.2	30.1	160.4	132.2	158.1	116.3	127.8	20.6		
Nb	ppm	39.4	36.5	41.6	192.1	159.6	164.9	36.5	226.6	174.8	208.2	156.2	166.6	26.6		
Ni	ppm	137.4	157.4	123.3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	56.2		
Rb	ppm	25.1	22.8	25.6	167.4	119.5	128.1	18.7	162.0	123.1	153.1	117.5	128.3	13.9		
Sr	ppm	577.2	551.8	596.7	15.5	7.3	37.6	502.1	43.7	12.8	12.1	27.5	18.9	507.0		
Th	ppm	2.8	2.9	3.4	23.7	15.4	15.8	23.0	23.0	15.2	20.6	15.3	16.3	1.5		
Y	ppm	27.5	26.6	28.6	125.5	133.4	143.6	44.3	169.3	153.2	175.1	128.2	140.9	25.2		
Zr	ppm	161.8	151.6	167.0	1240.3	1020.1	1057.3	168.3	1431.9	1092.9	1391.0	1023.6	1100.5	142.9		

**Table 2**  
Selected Glass Data for Aluto, Kone, and Fentale Volcanoes

Rock type	Relative age	Location	Sample												
			01-02-24	13-05-04	26-01-SMP	31-01-LE	F01	F11	F16	F17	F27	F42	F44	F48	K3.18
			Porphyritic obsidian	Welded ignimbrite	Porphyritic obsidian	Porphyritic obsidian	Porphyritic obsidian	Welded ignimbrite	Porphyritic obsidian	Pumice lapilli	Porphyritic obsidian	Pumice lapilli	Welded ignimbrite	Welded ignimbrite	Pumice lapilli
			Postcaldera	Caldera	Postcaldera	Postcaldera	Precaldera	Caldera	Postcaldera	Postcaldera	Precaldera	Postcaldera	Caldera	Caldera	Kone caldera
Lat. (N)			7.7698	7.8407	7.8161	7.7832	8.9978	8.9378	8.9584	8.9535	8.9776	8.9578	8.9577	8.9279	Kone caldera
Long. (E)			38.7471	38.7303	38.7773	38.8268	39.8709	39.8934	39.9271	39.9295	39.8733	39.8992	39.8986	39.8432	8.8178
SiO <sub>2</sub>	wt%		74.16	73.02	73.36	74.02	70.67	69.78	70.37	72.65	70.54	73.12	71.42	70.34	74.97
TiO <sub>2</sub>	wt%		0.28	0.31	0.16	0.26	0.55	0.49	0.20	0.51	0.54	0.53	0.42	0.31	0.14
Al <sub>2</sub> O <sub>3</sub>	wt%		10.16	9.20	8.95	9.09	9.58	9.48	11.98	8.87	9.48	9.11	8.76	11.20	8.68
FeO	wt%		5.33	6.49	6.86	6.27	8.03	8.69	5.31	7.60	8.09	7.54	8.22	6.23	8.79
MnO	wt%		0.27	0.26	0.38	0.33	0.43	0.39	0.23	0.36	0.41	0.35	0.39	0.29	0.32
MgO	wt%		bdl	0.02	bdl	bdl	0.02	0.01	0.03	0.01	0.01	bdl	0.02	0.02	bdl
CaO	wt%		0.20	0.19	0.20	0.23	0.28	0.52	0.15	0.41	0.33	0.37	0.35	0.21	0.19
Na <sub>2</sub> O	wt%		5.11	4.87	5.66	5.22	5.71	6.10	6.35	5.24	5.88	4.67	5.89	6.20	4.79
K <sub>2</sub> O	wt%		4.50	5.65	4.42	4.53	4.60	4.39	5.33	4.32	4.63	4.31	4.48	5.11	4.36
P <sub>2</sub> O <sub>5</sub>	wt%		bdl	bdl	0.02	0.05	0.13	0.16	0.04	0.02	0.10	bdl	0.07	0.06	bdl
Al <sub>2</sub> O <sub>3</sub>	wt%		1.31	1.54	1.57	1.49	1.50	1.56	1.35	1.50	1.55	1.36	1.66	1.40	1.10
Ba	ppm		367.2	107.9	393.4	370.5	694.2	679.5	292.3	853.3	856.9	482.1	652.6	525.7	247.3
Ce	ppm		198.9	290.7	324.8	267.1	210.2	190.4	323.8	270.0	236.3	299.5	200.5	239.0	357.3
La	ppm		98.5	149.4	162.1	134.1	104.9	91.6	166.5	136.8	117.9	151.3	99.2	122.7	177.6
Nb	ppm		132.9	240.5	212.8	177.8	152.5	124.6	258.5	179.2	163.1	212.8	137.3	165.3	230.1
Rb	ppm		101.1	117.7	147.9	126.6	118.9	17.1	198.7	141.2	126.5	168.8	114.3	128.6	147.3
Sr	ppm		4.7	4.3	6.8	5.8	8.3	9.5	14.6	10.9	13.2	12.5	10.0	9.7	4.5
Y	ppm		97.8	120.0	158.8	130.3	121.9	102.4	186.0	147.1	140.1	169.6	115.4	140.3	157.0
Zr	ppm		814.2	1387.5	1319.4	1085.7	890.0	780.1	1495.6	1019.4	952.6	1304.9	816.8	1007.1	1362.1
															1371.0

Note. Major elements were acquired via Electron Probe Micro-Analyzer at the Department of Earth Sciences at the University of Cambridge; trace elements were acquired via Secondary Ion Mass Spectrometry at the School of Geosciences at the University of Edinburgh. bdl = below detection limit (all values reported are above detection limits); A.I. = apatitic index (molar (Na<sub>2</sub>O + K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub>).



Table 1 (continued)

Rock type	Relative age	Sample													MER140Bb
		K3.30	K3.41	K4.10	K06	KBG25	KBN29	M057A	MER128A	M130A	MER133A	MER136A	MER137A	MER138A	
		Porphyrific obsidian	Pumice airfall	Porphyrific obsidian	Pumice lapilli	Porphyrific obsidian	Welded ignimbrite	Pumice lapilli	Pumice breccia	Pumice breccia	Basalt scoria	Basalt scoria	Basalt scoria	Basalt scoria	Welded ignimbrite
		Post-Kone caldera	Kone caldera	Pre-Kone caldera	Post-Kone caldera	Pre-Kone caldera	Kone caldera	Postcaldera	Kone caldera	Kone caldera	Post-Kone caldera	Post-Kone caldera	Post-Kone caldera	Post-Kone caldera	Kone caldera
Location	Lat. (N)	8.8691	8.8244	8.8628	8.8156	8.8000	8.8000	7.7865	8.7877	8.8091	8.8544	8.8239	8.8292	8.8418	8.8434
	Long. (E)	39.7250	39.6591	39.6640	39.6995	39.6920	39.6920	38.8098	39.6589	39.6873	39.7469	39.7047	39.7096	39.7139	39.7332
SiO <sub>2</sub>	wt%	70.53	75.22	71.36	72.91	70.75	70.43	75.37	75.55	75.45	48.95	47.40	47.69	47.56	73.17
TiO <sub>2</sub>	wt%	0.49	0.18	0.39	0.22	0.35	0.48	0.30	0.19	0.18	2.54	3.14	2.72	2.94	0.24
Al <sub>2</sub> O <sub>3</sub>	wt%	10.39	9.65	8.58	7.89	9.86	10.97	8.75	9.24	8.78	14.39	14.68	15.83	15.09	9.05
FeO	wt%	7.41	5.11	8.50	7.78	7.50	7.26	6.14	5.91	6.01	11.84	12.73	11.88	12.39	6.46
MnO	wt%	0.31	0.18	0.36	0.32	0.35	0.33	0.30	0.26	0.32	0.18	0.26	0.24	0.24	0.25
MgO	wt%	bdl	bdl	0.03	0.01	0.03	0.04	bdl	bdl	bdl	6.71	5.14	5.00	4.98	0.02
CaO	wt%	0.37	0.19	0.37	0.25	0.33	0.40	0.20	0.21	0.19	11.35	10.48	10.60	10.60	0.21
Na <sub>2</sub> O	wt%	5.89	5.03	5.95	6.23	6.11	5.31	4.75	4.23	4.73	2.45	3.90	4.04	4.01	5.61
K <sub>2</sub> O	wt%	4.55	4.44	4.42	4.39	4.66	4.65	4.20	4.23	4.32	0.99	1.51	1.39	1.44	4.91
P <sub>2</sub> O <sub>5</sub>	wt%	0.06	bdl	0.05	bdl	0.06	0.12	bdl	bdl	0.02	0.61	0.76	0.62	0.76	0.08
Al <sub>2</sub>	wt%	1.01	0.98	1.21	1.35	1.09	0.91	1.41	0.94	1.03	0.24	0.37	0.34	0.36	1.16
Ba	ppm	72.5	24.8	96.8	298.9	95.7	455.7	245.2	153.1	215.1	447.2	513.8	467.1	513.7	59.9
Ce	ppm	181.7	255.9	268.8	316.2	268.5	203.5	298.6	318.7	196.1	64.5	91.6	79.1	86.4	290.7
La	ppm	91.4	131.8	136.3	159.4	134.4	102.7	147.2	160.5	97.2	29.1	44.3	40.3	43.1	149.0
Nb	ppm	130.3	202.7	209.1	216.6	207.5	148.7	200.3	229.3	130.8	32.6	53.0	43.9	49.8	225.3
Rb	ppm	156.5	261.9	192.3	214.3	194.8	152.1	151.4	240.0	89.0	22.8	38.7	32.2	36.4	245.1
Sr	ppm	bdl	5.1	4.7	8.5	4.7	4.9	4.5	4.2	3.3	580.4	590.0	625.6	624.8	2.7
Y	ppm	102.1	138.8	158.3	175.2	158.2	104.3	132.8	154.0	91.0	30.4	37.1	30.8	34.6	159.5
Zr	ppm	828.2	1202.1	1296.4	1353.9	1287.8	903.4	1131.9	1374.3	768.6	158.1	224.0	191.5	210.7	1395.3

16% for  $K_2O$ ; accuracy of 19% for  $TiO_2$  and 8% for  $K_2O$ ) was achieved using a range of secondary standards. Standards compilations can be found in the supporting information.

Trace element analysis of matrix glasses was acquired by secondary ion mass spectrometry using a Cameca ims-4f ion probe at the School of Geosciences at the University of Edinburgh. Glass chips were handpicked from crushed material and mounted in epoxy blocks, which were then gold coated. A 25-mm square area was rastered with a low beam current prior to analysis to remove the gold coating and any contamination. A range of standards was used to construct a robust calibration and were analyzed at the beginning and end of every session to assess data quality. Precision of 4% and accuracy of 7% was achieved for all trace elements; Ba was measured with a precision of 1% and an accuracy of 7%; Zr with a precision and accuracy of 2%. Standards compilations can be found in the supporting information.

## 4. Results

### 4.1. Petrographic Descriptions

#### 4.1.1. Alkali Basalt

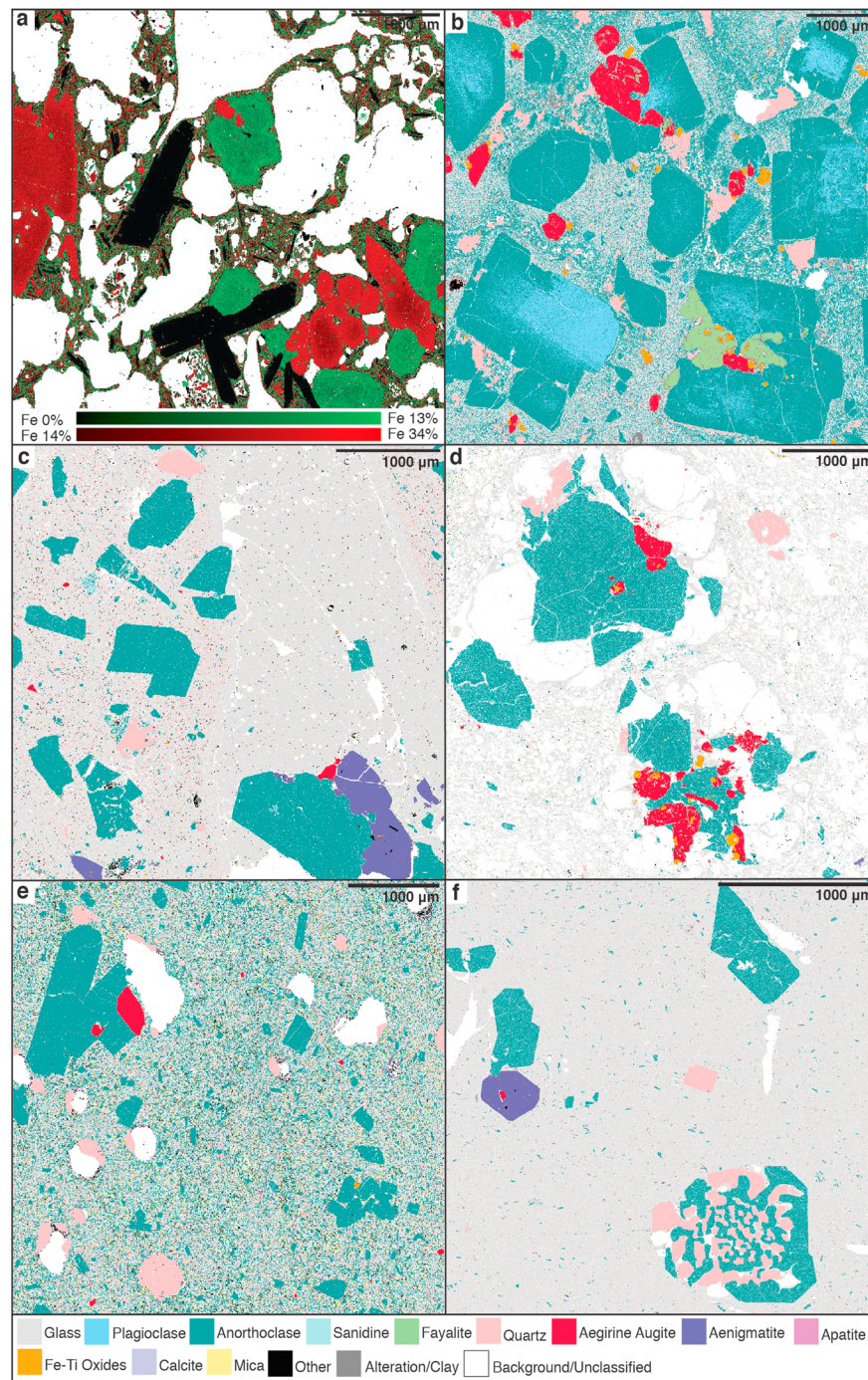
The alkali basalts are present as both porphyritic seriate lava and scoria (Figure 2a). Phenocrysts are typically up to a few millimeters in size and represent from 5.5 to 26 absolute volume % (vol%) of the scoria samples and up to 45 vol % of the lava samples. Phases include plagioclase, olivine and augite (modal proportions of the phenocrysts of 78%, 22%, and 0% for the lavas, and 40%, 35%, and 25% for the scoria). Glomerocrysts are common, at up to 4 mm across they mainly comprise olivine and plagioclase, although clinopyroxene (Figure 2a) is particularly common in the scoria. Zoning is present in all phases (Figure 2a), particularly associated with the glomerocrysts. Olivine and plagioclase phenocrysts show normal zoning, with rare occurrences of reverse-zoned olivine rims. Augite phenocrysts show oscillatory zoning. Chrome spinels are generally present in the groundmass of both the lava and scoria, and as inclusions within the phenocrysts.

#### 4.1.2. Caldera-Forming Eruptions

Large-volume ignimbrite eruptions are associated with caldera-forming phases at Aluto, Kone, and Fentale (Fontijn et al., 2018; Gibson, 1967, 1970, 1974; Giordano et al., 2014; Hutchison, Pyle, et al., 2016; Rampey et al., 2010, 2014). Samples selected for study are all intensely welded. Ignimbrite bulk compositions straddle the trachytic to rhyolitic boundary (Figure 3a) and are crystal rich, with phenocrysts accounting for 17 to 35 absolute volume % (Figures 2b and 2c). The crystal population is dominated (up to 85 modal % proportion of the phenocrysts) by broken euhedral feldspars up to 3 mm in size, which vary from oligoclase to anorthoclase to sanidine, with the former more abundant in the less evolved samples, the latter in the most evolved (Figures 2b and 2c). Some feldspars display normal zoning, with plagioclase cores (Figure 2b); occasional andesine (up to 5 modal %) is also present. Other phases include fayalite (up to 5 modal % in less evolved samples), with alteration rims, fractured quartz (up to 25 modal % in more evolved samples), rounded or elongate aegirine-augite (up to 10 modal %), and aenigmatite (up to 10 modal %). Most of these phases are up to 0.5 mm in size, but can reach up to 2.5 mm in size in some cases. The phenocrysts can form a glomeroporphyritic texture, with clots up to 5 mm in size (Figures 2b and 2c), set in a variably devitrified groundmass. Fe-Ti oxides are present as microphenocrysts, 0.1–0.2 mm in size, clustering in and around the glomerocrysts (Figure 2b). Xenoliths of rhyolite and trachyte lava are common, particularly in rhyolitic ignimbrites, as are finely crystalline fiamme and collapsed vesicles (Figure 2c). The unwelded pumiceous fall material, associated with caldera-forming eruptions, has a similar phase assemblage to the rhyolitic ignimbrites and shows similar textures (Figure 2d), although it has a lower phenocryst content (<10 vol %).

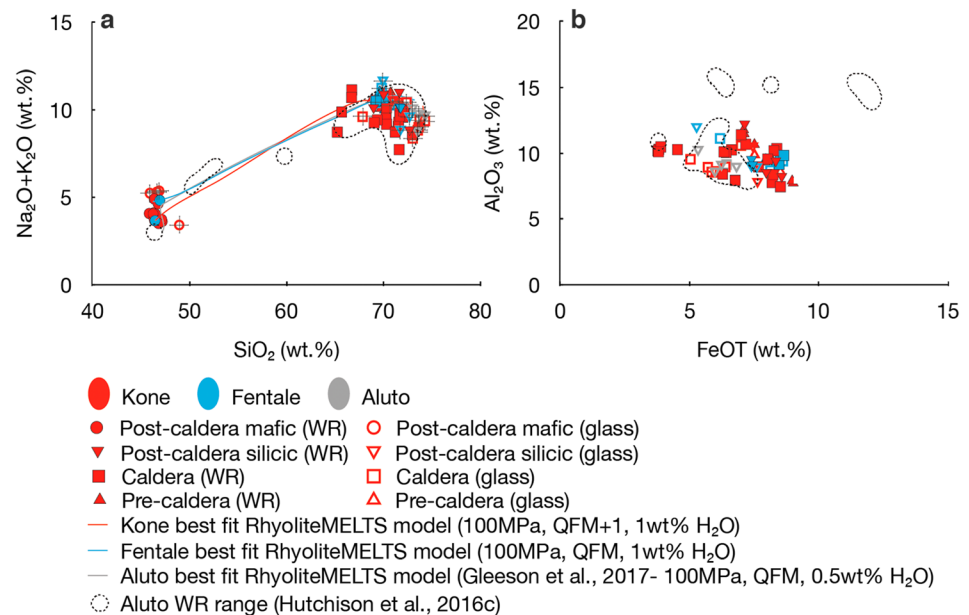
#### 4.1.3. Pre and Postcaldera Eruptions

Felsic lava and pumice is erupted during precaldern and postcaldern phases. Samples selected for study include pre-Birenti caldera, pre-Kone caldera, and post-Kone caldera lava from Kone, precaldern and postcaldern lava from Fentale, and postcaldern lava and pumice from Aluto. Trachytic lava, and occasional rhyolite lava, contains up to ~30 vol % phenocrysts (Figure 2e), dominated by euhedral sanidines (>70 modal %) up to 3 mm in size, and small rounded quartz crystals (up to 25 modal %) 0.2–0.3 mm in size. Aegirine-augite (<2.5 modal %) up to 2 mm in size, and fayalite (<2.5 modal %) up to 3 mm in size, with thick alteration rims, complete the phase assemblage. Glomeroporphyritic crystal clots are common (Figure 2e). The fine-grained (containing crystals up to 10  $\mu$ m in size) groundmass is made up of a similar assemblage. The rhyolite lava is dominantly aphyric, or crystal-poor porphyritic obsidian with <10 vol % crystals held in a glassy groundmass (Figure 2f). The phase assemblage is made up by euhedral phenocrysts of sanidine (70 modal %), rounded



**Figure 2.** QEMSCAN phase assemblage maps showing key petrological textures. The QEMSCAN software creates phase assemblage maps from data acquired from a combination of low-count energy-dispersive X-ray spectra and backscattered electron brightness and X-ray count information. From top left to bottom right: (a) Fe chemical map displaying the phase assemblage and petrological textures of a postcaldera basaltic scoria from Kone. Note the glomerocrystic clotting of phenocrysts, and zoned olivines (red) and clinopyroxene (green); (b) crystal-rich trachytic ignimbrite from Aluto, dominated by anorthoclase. Some crystals are normally zoned with plagioclase cores. Fayalite, aegirine augite, and microphenocrysts of Fe-Ti oxides form glomerocrystic clots with the feldspar. Quartz completes the assemblage; all is set in a devitrified groundmass; (c) crystal-rich rhyolitic ignimbrite from Kone, showing a large fiamme on the right. Dominated by anorthoclase, quartz, aegirine-augite and aenigmatite complete the phase assemblage, all set in a devitrified groundmass; (d) pumice lapillus from a Kone fall deposit associated with the caldera formation. The phase assemblage present is similar to related ignimbrites, dominated by anorthoclase. Aegirine augite and microphenocrysts of Fe-Ti oxides form glomerocrystic clots to give a similar texture; (e) trachytic precaldere lava from Kone, dominated by anorthoclase. Aegirine augite and Fe-Ti oxides are also present, forming glomerocrystic clots with the feldspar crystals. The fine-medium groundmass is dominated by quartz, alkali feldspar and aegirine augite; (f) a comparatively more crystal-poor rhyolitic lava from Aluto. The phase assemblage is dominated by anorthoclase, aenigmatite and aegirine augite. Complex granophyric intergrowths of alkali feldspar and quartz are common.





**Figure 3.** Whole-rock analyses of Kone and Fentale samples. Dashed fields show Aluto data coverage (Hutchison, Pyle, et al., 2016); glass analyses for the three volcanoes are shown by unfilled symbols. (a) Total alkalis versus silica diagram. The dashed line shows the alkaline-sub-alkaline divide of Irvine and Baragar (1971); (b) classification diagram of peralkaline rhyolites and trachytes (Macdonald, 1974). Colors are used to denote the three different volcanoes throughout the paper, shapes the relative age of deposits. Errors are smaller than symbols shown.

quartz (15 modal %), and elongate or rounded aegirine augite and aenigmatite (7 modal %), all up to 1 mm in size. Granophyric intergrowths of quartz and alkali feldspar are common (Figure 2f). At up to 2.5 mm in size, these intergrowths appear to nucleate around a grain showing dissolution textures and can contain inclusions of aegirine-augite. They may represent growth during rapid undercooling of melt compositions that are undersaturated with respect to quartz (Gleeson et al., 2017; Lowenstern et al., 1997). The glass matrix of the rhyolites contains aligned microlites of alkali feldspar and aegirine augite. Postcaldera pumice deposits are similar in assemblage and petrographic texture to the postcaldera rhyolite lavas, though generally have lower phenocryst contents (closer to aphyric).

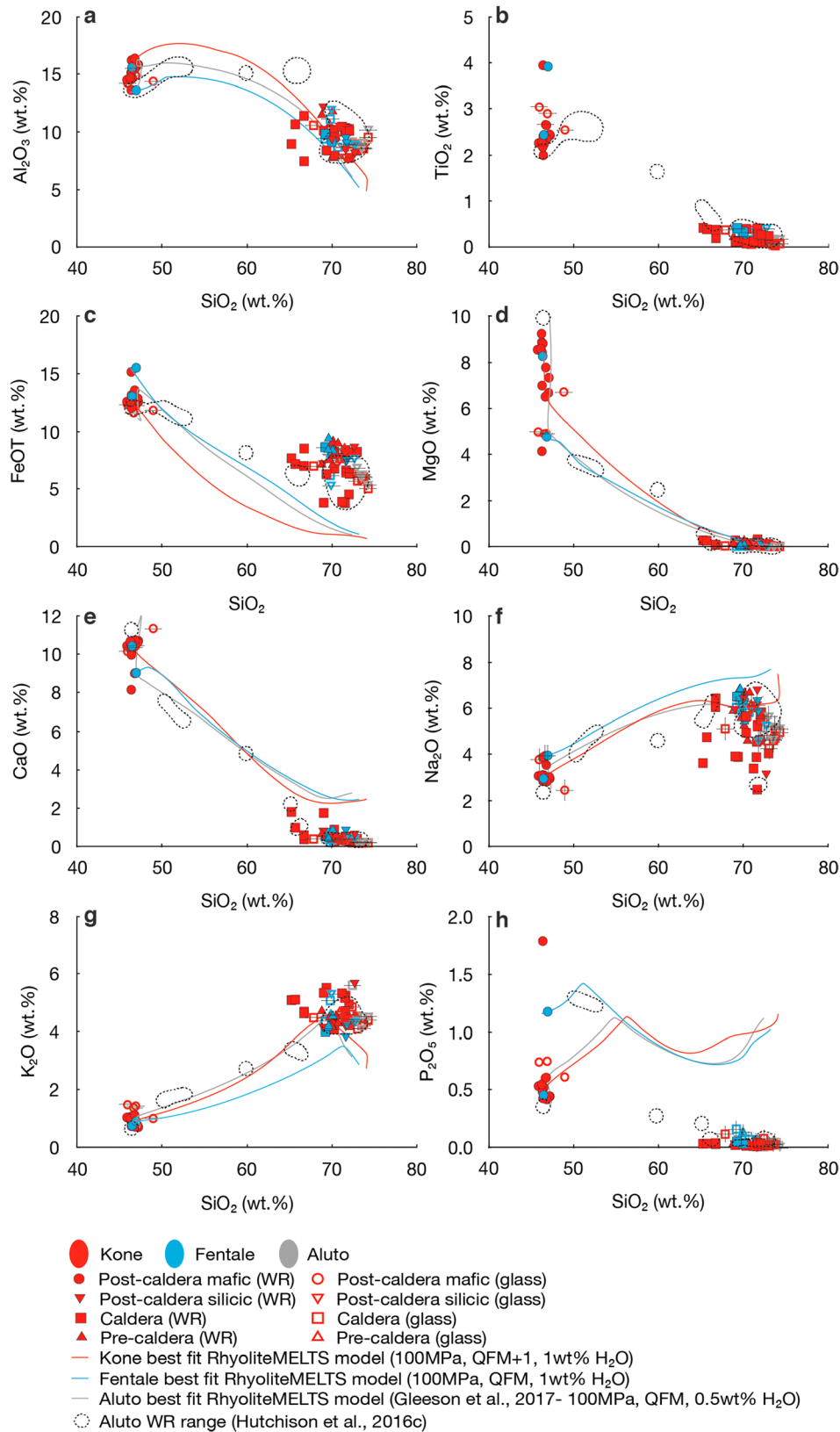
## 4.2. Whole-Rock and Glass Compositions

### 4.2.1. Major Elements

Whole-rock compositions for Kone and Fentale are presented in Table 1 and provided in supporting information S12 and S13; glass compositions for Aluto, Kone and Fentale are presented in Table 2 and provided in supporting information S14. Whole-rock compositions for Aluto volcanic products are presented by Hutchison, Pyle, et al. (2016) and are highlighted by fields marked out by dashed lines. Rocks were classified using the total alkalis-silica diagram (Figure 3a) after LeBas et al. (1986), and the  $\text{FeO}_t\text{-Al}_2\text{O}_3$  diagram (Figure 3b) after Macdonald (1974). There is a large range in silica content across the sample suite, although rocks of intermediate composition are absent, the data show a clear gap in compositions between ~50 and 60 wt%  $\text{SiO}_2$ , excepting rare examples of enclaves from Aluto (Hutchison, Pyle, et al., 2016). All of the evolved samples are peralkaline, with most classified as pantellerites based on their high FeO concentrations (Figure 3b; Macdonald, 1974). Some Aluto trachytic ignimbrites appear comenditic due to their raised  $\text{Al}_2\text{O}_3$  contents. The mafic samples have a transitional composition and straddle the alkaline-subalkaline divide of Irvine and Baragar (1971; Figure 3a).

Both the glass and whole-rock data show that increasing  $\text{SiO}_2$  content correlates with an increase in alkalis and a decrease in ferromagnesian, Ca and Ti oxides (Figure 4). This trend is indicative of protracted fractional crystallization controlled by removal of olivine, clinopyroxene, plagioclase, Fe-Ti oxide, quartz, alkali feldspar, and aenigmatite (in approximate order of appearance).  $\text{K}_2\text{O}$  shows a smooth, largely linear increase





**Figure 4.** Harker variation diagrams (a-h) of whole-rock and glass major element compositions. Dashed fields show Aluto whole-rock data coverage (Hutchison, Pyle, et al., 2016); solid lines show melt composition predicted by the best fit RhyoliteMELTS models (Gleeson et al., 2017; Gualda et al., 2012). Errors are smaller than symbols shown.

(Figure 4g).  $\text{Al}_2\text{O}_3$  shows flat but scattered levels before a step-change at  $\sim 68$  wt. %  $\text{SiO}_2$ , where it decreases to 7.5–12 wt. % in the pantellerite samples, reflecting the dominance of alkali feldspar fractionation (Figure 4a).  $\text{Na}_2\text{O}$  shows an increasing trend with  $\text{SiO}_2$  up to the trachytic compositions, then displays considerable variation (2.5–7 wt. %) within the pantellerites (Figure 4f). The variation in  $\text{Na}_2\text{O}$  after  $\sim 70$  wt. %  $\text{SiO}_2$  reflects the dominance of alkali feldspar as the fractionating phase, though it should be noted that glass alteration and Na loss may also be important. By comparing the FK/A indicator of peralkalinity (mol  $(\text{Fe} + \text{K})/\text{Al}$ ) to that of the agpaitic index (mol  $(\text{Na} + \text{K})/\text{Al}$ ), several Kone samples, namely the silicic glasses, are identified as likely to have undergone Na loss (see supporting information S1; White et al., 2003). Hutchison, Pyle, et al. (2016) examined Na loss at Aluto in samples collected from isolated pumice cones that would have been located at the edge of the lake during lacustrine high stands, leading them to suggest that postemplacement alteration processes (e.g., leaching by surface water interaction) may be the causal factor. Na loss has also been identified in pumice from Rungwe, Tanzania, Fontijn et al. (2013) suggest that the combination of high vesicularity, increasing exposed surface area, and the climate contributes to the alteration.

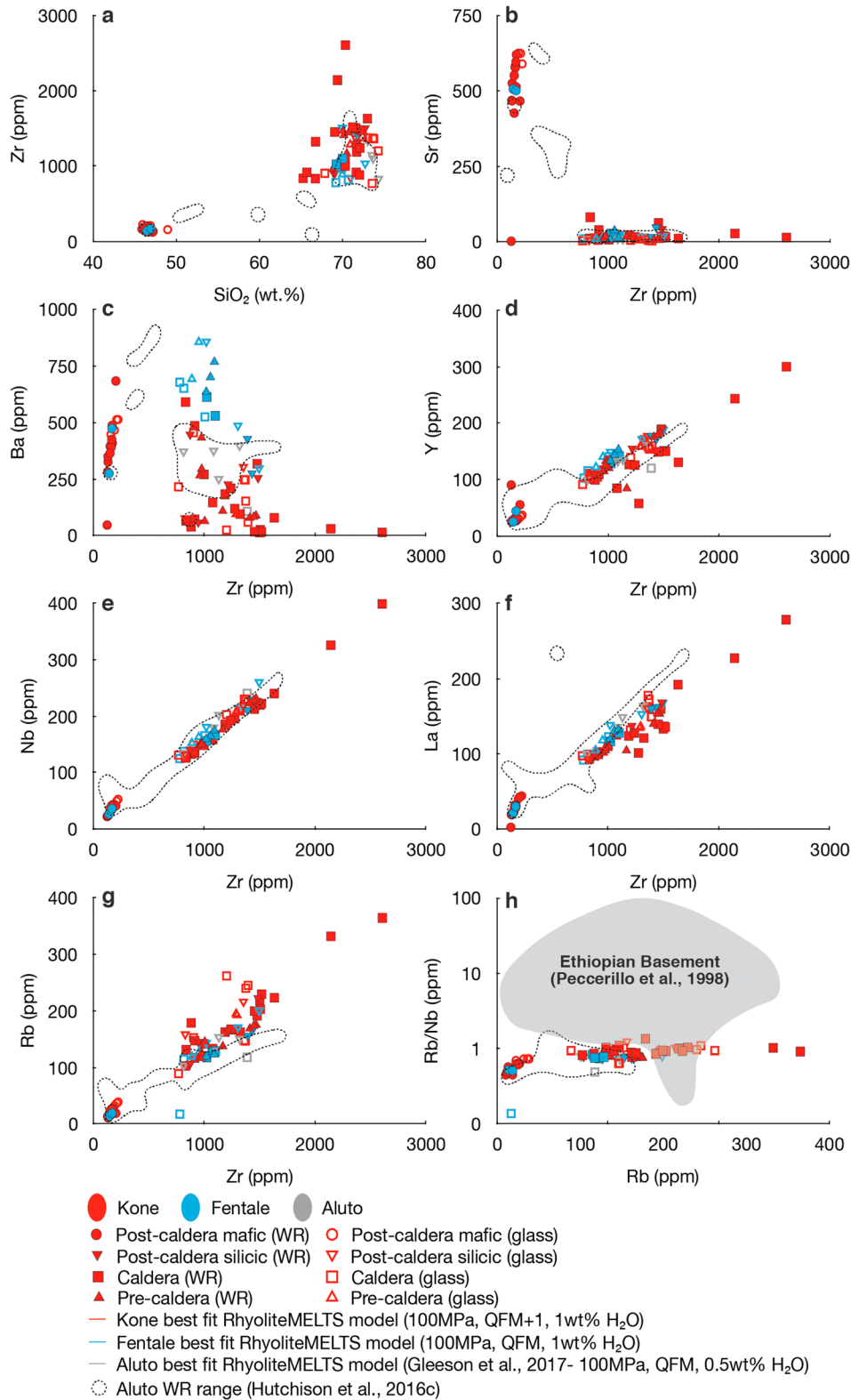
While the glass and whole-rock data are generally tightly coupled, the glass data show slightly lower  $\text{MgO}$  and  $\text{FeO}$ , and higher  $\text{TiO}_2$  and  $\text{K}_2\text{O}$  at the mafic end of the spectrum, and higher  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  at the silicic end of the spectrum, particularly compared to whole-rock analyses of the crystal-rich ignimbrites. This likely reflects the presence of retained, large olivine phenocrysts in the basalts, and alkali feldspar phenocrysts in the pantellerites. Peralkaline melts become increasingly sodic as they evolve due to the “orthoclase effect” (Bailey & Schairer, 1964). Gibson (1974) identified significant geochemical variation between Fentale precaldere and postcaldere pantellerites; this study replicates that with postcaldere samples showing higher  $\text{SiO}_2$  and lower  $\text{TiO}_2$ ,  $\text{FeO}$ , and  $\text{MnO}$  contents noted in both the whole-rock and glass data. No such pattern was observed for the Kone samples.

Best fit RhyoliteMELTS models (Gualda et al., 2012) for Kone and Fentale were determined using least squares residual analysis (following the method of Gleeson et al., 2017); these are plotted as solid lines, along with the model for Aluto determined by Gleeson et al. (2017; Figures 3 and 4). The models provide a good first-order fit to the geochemical data, but deviation is observed for more evolved (pantelleritic) compositions. There is a departure of the model from  $\text{FeO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{P}_2\text{O}_5$  glass and whole-rock compositions (Figures 4c, 4e, and 4h) and consequently the model overestimates peralkalinity substantially for the rhyolites with  $\text{SiO}_2 > 70$  wt. %. Overprediction of  $\text{P}_2\text{O}_5$  and  $\text{CaO}$  is likely related to inaccuracies in the stabilization of apatite and other mineral phases for which Rhyolite-MELTS is not calibrated (Rooney, Hart, et al., 2012). Underprediction of  $\text{FeO}$  content reflects the limited constraint on aenigmatite stability (Hutchison et al., 2018). Rooney, Hart, et al. (2012) highlight the lack of experimental constraints on the stability of F-bearing phases in thermodynamic models for peralkaline systems.

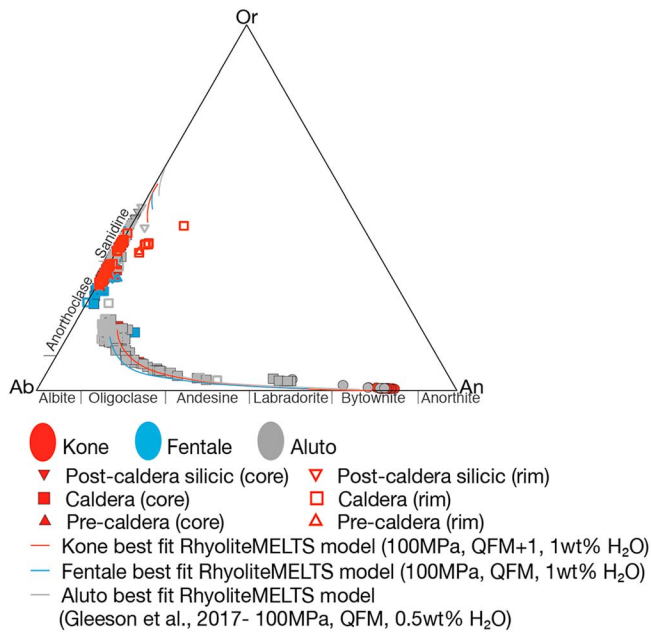
#### 4.2.2. Trace Elements

The covariation of selected trace elements with Zr, which is highly incompatible in peralkaline melts (Figure 5a), is shown in Figure 5. Compatible elements show a negative correlation with Zr (Figures 5b and 5c); incompatible elements show a positive correlation. Incompatible-incompatible trace element diagrams (Figures 5d–5g) show linear positive trends that pass through the origin and are consistent with the most evolved compositions at Aluto, Kone, and Fentale being derived from a mafic parent similar to those sampled. Incompatible element ratios such as  $\text{Rb}/\text{Nb}$  (Figure 5h) do not show significant variability across the sample suite.  $\text{Rb}/\text{Nb}$  ratios are generally lower in the sample suite than that of the Precambrian crustal rocks (Peccerillo et al., 1998), which likely represent a component of the basement rocks.

Glass and whole-rock compositions are tightly coupled. Ba contents deviate from the other elements analyzed, showing an increase in concentrations up to trachytic compositions, and then considerable variation (12–850 ppm) within the pantellerites (Figure 5c), marking the appearance of alkali feldspar as a major fractionating phase. There is no clear relationship between the Ba concentrations observed in the whole rock and in glass (Figure 5c). Given the textural evidence of glomerocrystic clots of feldspar phenocrysts, this may indicate accumulation of trace-element-enriched feldspar crystals (see section 5.3). Again, this study confirms the result of Gibson (1974), identifying differences between the trace element geochemistry of Fentale precaldere and postcaldere pantellerites. Postcaldere samples have higher



**Figure 5.** Whole-rock and glass trace element compositions plotted against Zr concentration (b-h) due to its incompatibility (a). Dashed fields show Aluto whole-rock data coverage (Hutchison, Pyle, et al., 2016); shaded field shows Precambrian crustal rock geochemistry (Peccerillo et al., 1998), which likely represent a component of the basement rocks. Key as in Figure 3. Errors are smaller than symbols shown.



**Figure 6.** Feldspar classification ternary diagram, solid lines show feldspar compositions predicted by the best fit RhyoliteMELTS models (Gleeson et al., 2017; Gualda et al., 2012).

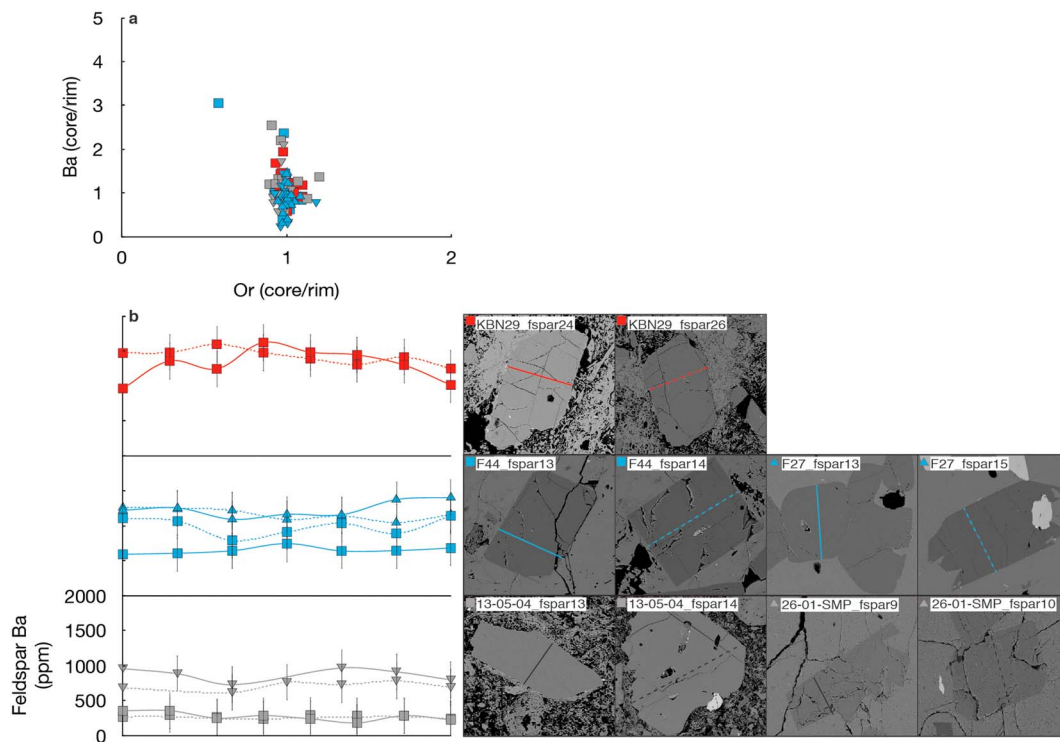
whole-rock and glass concentrations of incompatible elements such as Y, Nb, La, and Rb, but lower concentrations of Ba. No such pattern was observed for the Kone samples.

### 4.3. Feldspar Compositions

Plagioclase compositions in the Aluto samples include bytownite and labradorite ( $An_{55-81}$ ;  $Ab_{42-18}$ ;  $Or_{1-3}$ ), while Kone samples are dominated by bytownite ( $An_{80-84}$ ;  $Ab_{19-15}$ ;  $Or_{0-1}$ ; Figure 6). Aluto trachytes contain feldspars that straddle the oligoclase/anorthoclase boundary ( $An_{5-42}$ ;  $Ab_{77-56}$ ;  $Or_{3-24}$ ), with some rare andesine cores. Kone and Fentale samples contain minor amounts of these feldspars ( $An_{11-20}$ ;  $Ab_{73-72}$ ;  $Or_{8-18}$ ). Alkali feldspars at Aluto are predominantly sanidine ( $An_{0.1-0.4}$ ;  $Ab_{68-50}$ ;  $Or_{32-65}$ ), while at Kone and Fentale they straddle the anorthoclase/sanidine boundary ( $An_{0.1-3}$ ;  $Ab_{76-54}$ ;  $Or_{24-46}$ ). While some anorthoclases in both Kone and Aluto caldera-forming eruptive deposits display normal zoning, with more albitic cores (Figure 2b), most show no apparent zoning (Figures 2c–2f and 7a and 7b); the range from core to rim is typically <3 mol% for Or and Ab. The feldspar analyses can be found in Table 3 and supporting information S15 and S16.

The predicted feldspar compositions from the best fit RhyoliteMELTS models (Gleeson et al., 2017; Gualda et al., 2012) are shown plotted as solid lines on Figure 6. They provide a good first-order fit to the geochemical data, following the smooth curve displayed by the observed plagioclase

data closely. However, RhyoliteMELTS fails to accurately predict the composition of the alkali feldspars, over-predicting Or contents. The modeled fractionation of more potassic feldspars results in RhyoliteMELTS over-estimating peralkalinity, as the influence of the orthoclase effect (Bailey & Schairer, 1964) is inflated.



**Figure 7.** Feldspar trace element compositions are highly variable, to investigate the presence/absence of zoning plot (a) shows Ba and Or concentration in the core of the alkali feldspar normalized by the concentration of Ba and Or in the rim, while (b) shows selected Ba profiles across a number of crystals from Kone, Fentale, and Aluto. Key as in Figure 6.



**Table 3**

Selected Feldspar Data for Aluto, Kone, and Fentale Volcanoes Acquired via EPMA at the Department of Earth Sciences at the University of Cambridge

			Concentration (ppm)				Partition coefficients	
Sample	<i>n</i>	<i>X</i> <sub>An</sub> , <i>X</i> <sub>Ab</sub> , <i>X</i> <sub>Or</sub>	Ba mean	Ba min	Ba max	Ba σ	<i>D</i> <sub>Ba</sub>	σ
Plagioclase								
13-05-04	1	An(37-42), Ab(60-56), Or(3-3)	2,002	1,691	2,313	440	N/A	N/A
18-11-07	45	An(5-39), Ab(77-58), Or(3-24)	2,875	920	4,061	775	N/A	N/A
MER140Bb	3	An(11-20), Ab(73-72), Or(8-18)	3,439	3,114	3,745	316	N/A	N/A
Alkali feldspar								
31-01-LE	6	An(0.1-0.4), Ab(65-58), Or(35-65)	1,216	676	2,443	496	3.56	1.52
26-01-SMP	10	An(0.1-0.3), Ab(60-50), Or(40-50)	800	489	2,230	290	2.16	0.44
13-05-04	12	An(0.1-3), Ab(68-57), Or(32-43)	466	182	2,350	421	6.37	5.12
F01	7	An(0.2-0.5), Ab(71-69), Or(28-31)	1,535	1,218	1,987	267	2.35	0.33
F16	7	An(0.1-0.2), Ab(63-55), Or(37-45)	562	244	872	190	2.07	0.68
F27	15	An(0.1-0.5), Ab(71-66), Or(28-33)	1,196	769	2,681	303	1.39	0.35
F44	12	An(0.1-2), Ab(76-61), Or(24-39)	1,467	405	4,064	853	2.80	1.4
F48	6	An(0.1-1), Ab(73-63), Or(26-37)	1,041	347	2,061	653	2.83	1.2
K04	2	An(0.3-0.3), Ab(70-68), Or(30-32)	575	420	728	160	N/A	N/A
K05	3	An(0.1-0.3), Ab(68-66), Or(30-34)	443	309	778	155	N/A	N/A
KBN29	21	An(0.2-3), Ab(71-64), Or(29-35)	1,477	835	2,790	410	3.06	0.92
M057A	3	An(0.1-0.4), Ab(62-54), Or(38-46)	680	510	923	149	3.24	0.47
M140Bb	2	An(0.1-0.1), Ab(66-60), Or(34-40)	637	331	1,044	340	9.35	5.41

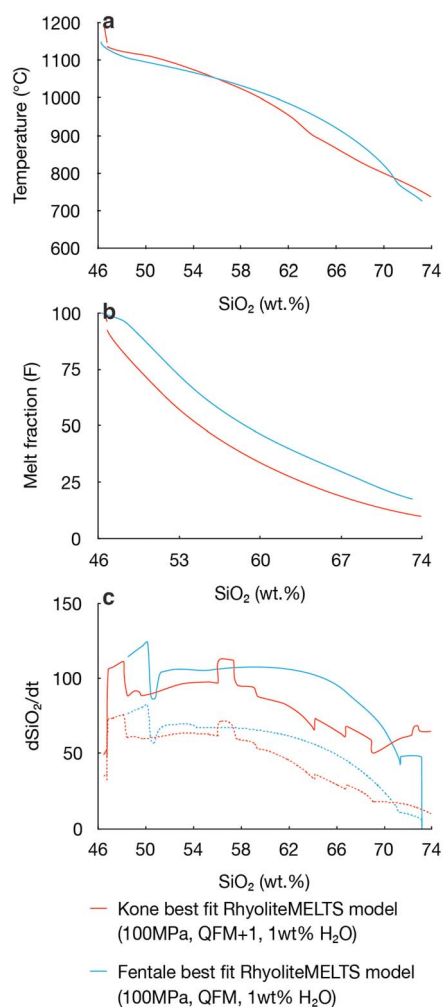
*Note.* Partition coefficients given are the average “apparent” partition coefficients calculated from feldspar rim and corresponding glass compositions.  $n$  = number of crystals analyzed (typically one analysis of plagioclase crystals, two analyses representing core and rim sections of the crystal for alkali feldspars);  $X_{An}$  = anorthoclase content;  $X_{Ab}$  = albite content;  $X_{Or}$  = orthoclase content; N/A = partition coefficients not calculated (due to lack of glass and/or feldspar rim compositions). EPMA = Electron Probe Micro-Analyzer.

Ba concentrations were used to assess trace element variation in the feldspars from the evolved rocks as Ba partitions strongly into the mineral phase and, unlike Sr, was observed above detection limits in most cases for the alkali feldspars. Data are presented in Table 3. The oligoclase and anorthoclase plagioclase feldspars typically contain the highest Ba concentrations, reaching >4,000 ppm Ba. Alkali feldspar Ba contents are highly variable at the individual sample scale for each of the volcanoes investigated, with an average standard deviation of 339 ppm for the Aluto samples, 266 ppm for the Kone samples, and 453 ppm for the Fentale samples. It should be noted that every sample also contained feldspars with Ba concentrations below the detection limits so the actual variation is larger. Individual samples contain feldspars with a standard deviation in Ba concentration of up to 853 ppm, with Ba concentrations varying between several hundred parts per million and >4,000 ppm. Variation in Ba concentrations tends to be greatest within the samples erupted during caldera-formation; and these samples also contain the most crystals with Ba concentrations above detection limits. Evidence for zoning was limited within the alkali feldspars (Figures 7a and 7b). Where zoning in major elements exists there is no systematic change in Ba contents from core to rim (Figure 7a). The limited amount of zoning observed may have been acquired from a range of processes (i.e., feldspar growth in a progressively evolving liquid, diffusive re-equilibration of crystals scavenged from a geochemically distinct region). Only the rims, and their relationship to their carrier liquids, are examined further in this study (note that in most cases the rims and cores are identical; Figure 7).

## 5. Discussion

### 5.1. Magma Compositions Are Dominated by a Fractional Crystallization Signature

As has been proposed in previous studies (e.g., Giordano et al., 2014; Hutchison, Pyle, et al., 2016; Hutchison et al., 2018; Macdonald et al., 2011; Peccerillo et al., 2003), the whole-rock and glass data are consistent with pantelleritic magmas being derived via extreme fractional crystallization of a basaltic parental melt. Following the method of Gleeson et al. (2017) for Aluto (for full details see supporting information S2 and S3), least squares residual analysis was used to find the best fit RhyoliteMELTS models (Gualda et al., 2012) for Kone and Fentale, using basalts from these volcanoes as starting compositions (samples MER133A and F12). There are a number of initial conditions which appear to provide a reasonably good match to the compositional data; however, results of the statistical analysis indicate that fractional crystallization at low-pressure



**Figure 8.** Melt  $\text{SiO}_2$  predicted by best fit RhyoliteMELTS models (Gualda et al., 2012) for Kone and Fentale volcanoes against (a) the predicted melt temperature, (b) the predicted liquid fraction ( $F$ ), and (c) the relative rates of differentiation (change in silica content with respect to time), estimated from RhyoliteMELTS output at wall rock temperatures of 500  $^{\circ}\text{C}$  (solid lines) and 700  $^{\circ}\text{C}$  (dashed lines).

conditions (100 MPa),  $f\text{O}_2$  at the QFM-QFM + 1 buffer, and an initial water content of  $\sim 1$  wt% offer the best fit RhyoliteMELTS models for Kone and Fentale volcanoes. This is consistent with the best fit model presented by Gleeson et al. (2017) for Aluto, and with findings for other peralkaline centers along the MER and globally (e.g., Barberi et al., 1975; Gasparon et al., 1993; Hutchison et al., 2018; Peccerillo et al., 2003; Neave et al., 2012; Rooney, Hart, et al., 2012).

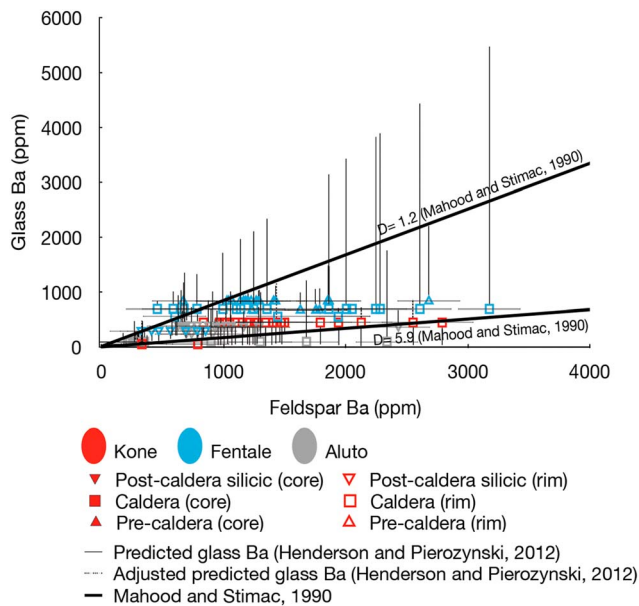
Some authors have suggested that peralkaline magmas may be generated by melting of preexisting basaltic rocks (Beard & Lofgren, 1991; Garland et al., 1995; Hay & Wendlandt, 1995; Thy et al., 1990). However, trace element ratios are constant through the differentiation suite and are also much lower than those of the local Precambrian crust (Figure 5h). Peccerillo et al. (2003) suggest that partial melting of crustal rocks would tend to increase melt large ion lithophile and high field strength element ratios (e.g., Rb/Nb) making it unlikely that there has been significant contribution from crustal assimilation. Hutchison et al. (2018) used Sr-Nd-O isotope systematics to rule out major crustal assimilation at both Kone and Aluto, consistent with these findings.

## 5.2. Implications for Our Understanding of Daly Gap Formation

There is a total absence of eruption deposits at Kone and Fentale with the intermediate magma compositions which are predicted to form during protracted fractional crystallization. This compositional gap is often referred to as the “Daly Gap” (Daly, 1925) and has also been noted at Aluto (Gleeson et al., 2017; Hutchison, Pyle, et al., 2016) where only rare enclaves, thought to be the product of magma mixing (Hutchison, Pyle, et al., 2016), have intermediate compositions. The Daly Gap has been observed at other sites along the MER (Peccerillo et al., 2003; Ronga et al., 2010; Rooney, Hart, et al., 2012), and at other peralkaline systems globally (Neave et al., 2012; White et al., 2009). The Daly Gap is often used to argue against derivation of peralkaline liquids by protracted fractional crystallization (e.g., Chayes, 1963, 1977). Despite this challenge, the feldspar data collected for Aluto, Kone, and Fentale preserve evidence for crystallization of magmas of intermediate composition somewhere in the storage system. The smooth change in feldspar major element compositions observed in the samples analyzed is further supported by the RhyoliteMELTS simulations of fractional crystallization, which closely replicate plagioclase feldspar evolution (Figure 6). The majority of the andesine

and oligoclase analyses were taken from resorbed feldspar cores, rimmed by more potassic compositions (Figures 2b and 2c), providing geochemical evidence for crystallization of intermediate magmas prior to melt evolution. White et al. (2009) described anorthoclase phenocrysts from trachytes erupted at Pantelleria with similar plagioclase composition cores, suggesting that they may have formed from benmoreitic magmas, trapped in lower, dense and viscous portions of the storage system by a trachytic “trap” zone. The “filtering” effects of density stratified peralkaline magma reservoirs have previously been cited as a mechanism for “Daly Gap” formation at Aluto (Gleeson et al., 2017), as well as Gedemsa (Peccerillo et al., 2003) volcano in the MER. Careful examination of the Fentale welded tuff by Gibson (1974) has revealed that it was erupted from a compositionally and therefore likely density-stratified storage region.

The best fit RhyoliteMELTS models for Aluto (Gleeson et al., 2017), Kone, and Fentale suggest, in addition, that these compositions may be physically scarce, with fractionating magmas passing rapidly through the intermediate stages. The models show that  $\text{SiO}_2$  does not vary linearly with temperature (Figure 8a) or melt fraction ( $F$ ; Figure 8b), which corresponds to the degree of crystallization ( $1 - F$ ). Mushkin et al. (2002) presented an equation for estimating the rate of change of differentiation:



**Figure 9.** Plot showing observed feldspar Ba contents against observed glass Ba contents. Partition coefficients calculated based on the experimental work of Henderson and Pirozynski (2012) have been used to predict glass Ba concentrations based on feldspar rim compositions (solid lines). Dashed lines show where adjusted values of NKA have been used in the calculation due to probable  $\text{Na}_2\text{O}$  loss. Melt Ba contents based on the observed partition coefficients of Mahood and Stimac (1990) are also indicated by the thick solid lines. Errors in feldspar Ba content are displayed by horizontal lines, errors in glass Ba content were smaller than the symbols shown.

maintain alkali feldspar compositions at around  $\text{Or } 35 \pm 5\%$  for evolved peralkaline melts (Bailey, 1974; Bailey et al., 1974; Bailey & Schairer, 1964; Carmichael & MacKenzie, 1963; Nicholls & Carmichael, 1969; Thompson & MacKenzie, 1990), the trace element contents of the feldspars are expected to vary as crystallization continues owing to the relatively large changes in trace element concentrations in melts during crystallization (and changing partitioning behavior with temperature and melt composition). Therefore, detailed trace element analysis is needed in order to reveal the true complexity of feldspars in these systems.

Ba partitioning between feldspar and peralkaline silicate melt depends largely on temperature and melt composition (in particular peralkalinity; Henderson & Pirozynski, 2012). It has been suggested that Ba feldspar-melt partition coefficients drop steeply with peralkalinity, despite the accompanying modest increases in  $\text{SiO}_2$  and drop in temperatures (Henderson & Pirozynski, 2012; Mahood & Stimac, 1990). This is due to increasing melt  $\text{SiO}_2$  content being accompanied by a decline in network-forming Al and an increase in Fe content, leading to Ba becoming very incompatible in feldspar crystals in highly evolved peralkaline melts. Here we have predicted melt Ba contents from the observed feldspar rim trace element geochemistry. Ba alkali feldspar-melt partition coefficients ( $D_{Ba}$ ) are based on equation 2 from the experimental work of Henderson and Pirozynski (2012):

$$\ln(D_{Ba}) = 37.8 - 0.06\text{NKA} - 0.037T, \quad (2)$$

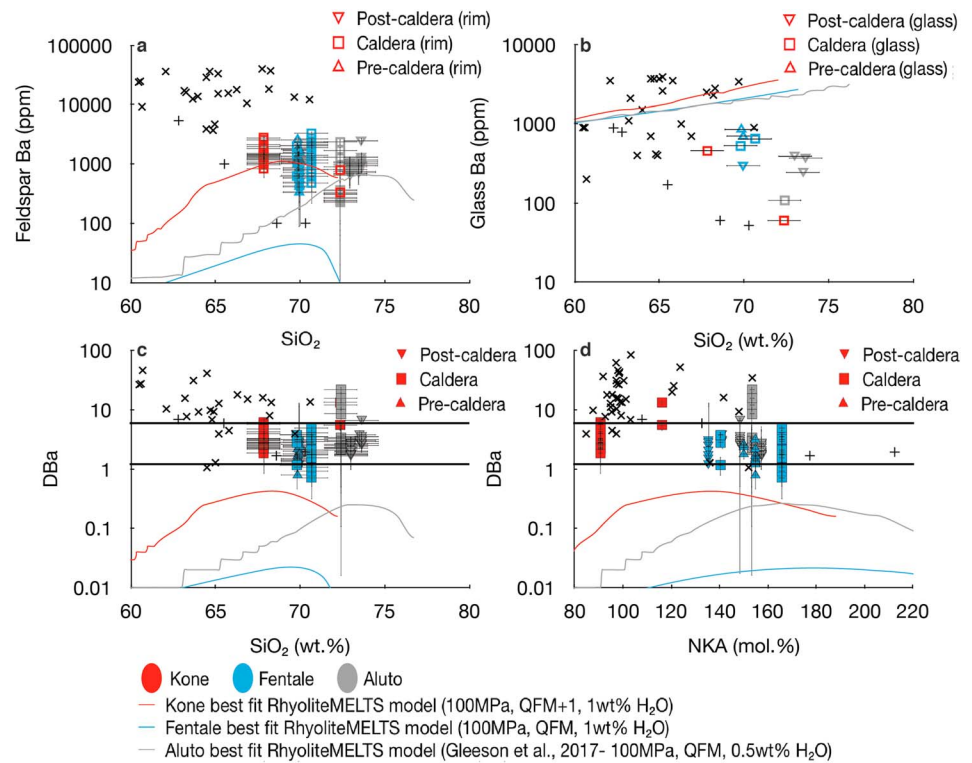
where NKA is the glass peralkalinity ( $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3$ , mol%) and temperature was set at  $765^\circ\text{C}$  (Gleeson et al., 2017). Figure 9 shows that in many cases the predicted melt Ba value is much higher than that of the observed, indicating that the feldspars are not in equilibrium with their carrier melt. As the partition coefficients calculated by this method are strongly dependent on melt peralkalinity it should be again be noted that several Kone samples may have low NKA due to Na loss (supporting information S1; White et al., 2003). Partition coefficients calculated for these samples may therefore be much higher than the true values and will produce lower predicted melt Ba concentrations. An adjusted value, based on the relationship

$$\frac{\partial \text{SiO}_2}{\partial t} \propto \frac{\partial \text{SiO}_2}{\partial H} (T_m - T_0) V^2, \quad (1)$$

where  $\frac{\partial \text{SiO}_2}{\partial t}$  is the rate of change of  $\text{SiO}_2$ ,  $H$  is the released heat at each melt temperature ( $T_m$ ), and  $V$  is the melt volume. The wall rock temperature ( $T_0$ ) has been varied as it is not output from the RhyoliteMELTS models. The models predict that faster rates of differentiation occur between  $\sim 50$  and  $\sim 65$  wt%  $\text{SiO}_2$  (Figure 8c). This has been suggested as the result of separation of  $\text{SiO}_2$ -poor minerals over this narrow interval (Clague, 1987; Gleeson et al., 2017; Peccerillo et al., 2003). This rapid differentiation may aid preservation of the plagioclase feldspar cores observed at Aluto, Kone, and Fentale, with timescales too short for complete re-equilibration. The occurrence of the Daly Gap is likely due to a combination of factors, including the predicted scarcity of intermediate compositions produced during fractionation, and the density stratification of zoned storage systems that may keep potentially crystal-rich zones of intermediate magmas locked away.

### 5.3. Heterogeneous Crystal Cargoes: Evidence for Entrainment of Antecrysts

While the whole-rock and glass geochemistry displays clear trends related to fractional crystallization, there is significant heterogeneity in the trace element composition of the feldspars (Figure 9). The Ba concentrations in the rims of individual feldspars within a sample can vary greatly, reflected in the unsystematic divergence between whole-rock and glass measurements of feldspar compatible traces such as Ba (Figure 5c). This suggests that a portion of the feldspars are antecrystic, particularly within the crystal-rich ignimbrite samples, where glomerocrystic clots of crystals, consistent with this interpretation, are prevalent. While phase equilibria will



**Figure 10.** Plots showing (a) feldspar and (b) glass Ba concentrations against glass SiO<sub>2</sub>. “Apparent” feldspar-melt Ba partition coefficients are shown against glass SiO<sub>2</sub> (c) and NKA (d). Solid lines depict the result of models based on the liquid line of descent from best fit RhyoliteMELTS models (Gleeson et al., 2017; Gualda et al., 2012) in tandem with a parameterization of the feldspar-melt partition coefficient based on peralkalinity and temperature (after Henderson & Pirozynski, 2012). Thick black lines (c and d) represent the minimum and maximum observed partition coefficients presented by Mahood and Stimac (1990). Experimental data from Henderson and Pirozynski (2012) are also plotted, along with observed values from Mahood and Stimac (1990).

between the FK/A and agpaitic index indicators of peralkalinity (White et al., 2003) has also been used in these calculations, producing more reasonable predicted melt Ba in these cases. Melt Ba contents based on the “effective” partition coefficients, observed in natural samples, of Mahood and Stimac (1990) are also indicated by the thick solid lines. The lower  $D_{Ba}$  of 1.2 is largely consistent with the relationship between the observed feldspar and melt Ba contents, however the higher  $D_{Ba}$  of 5.9 given by Mahood and Stimac (1990) again predicts much higher melt Ba contents based on the feldspar rims.

Ba partitioning behavior between alkali feldspars and melt, as constrained by Henderson and Pirozynski (2012), was also used to produce a simple fractional crystallization model based on RhyoliteMELTS simulations (Gualda et al., 2012) of the liquid line of descent (shown in Figures 3 and 4). Partition coefficients are calculated using equation (2) for each major element melt composition produced by RhyoliteMELTS, which are then converted to bulk partition coefficients using the mineral assemblages output by RhyoliteMELTS, assuming negligible intake of Ba by phases other than feldspar. This bulk partition coefficient is then input into a fractional crystallization equation:

$$\frac{C_i^l}{C_i^o} = (1 - X)^{D-1}, \quad (3)$$

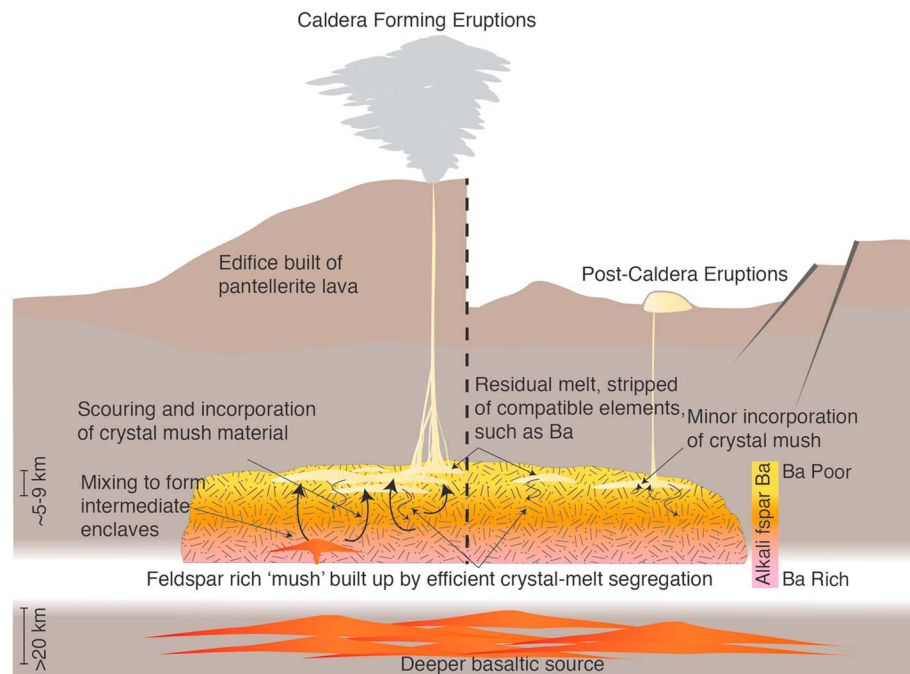
where  $i$  is the element of interest,  $C^o$  is the original concentration in the parental liquid, taken from the Ba contents of the starting basalts input into RhyoliteMELTS (17-01-05 for Aluto, MER133A for Kone, F12 for Fentale),  $C^l$  is the concentration in the liquid,  $D$  is the solid-melt partition coefficient,  $F$  is the melt fraction, and  $X$  is the fraction of material crystallized.



The results of the modeling are shown in Figure 10, along with the observations from the Aluto, Kone, and Fentale samples, and the experimental glasses on which the Ba feldspar-melt partitioning behavior is based (Henderson & Pirozynski, 2012) as well as some natural Ba data for pantellerite samples (Mahood & Stimać, 1990). The feldspar-melt partition coefficients for Ba ( $D_{Ba}$ ), predicted by RhyoliteMELTS combined with the empirical Ba partitioning behavior described by Henderson and Pirozynski (2012), extend only up to 0.5 for the evolved compositions investigated, quickly dropping again as the  $\text{SiO}_2$  content, and consequently the peralkalinity, increases (Figures 10c and 10d). These very low partition coefficients mean that the model predicts the Ba content of the melt to rise rapidly (Figure 10b) and feldspar Ba contents to peak at only 1,000 ppm (Figure 10a). The Fentale model predicts much lower values for  $D_{Ba}$ , and consequently the feldspars too. However, it is likely that these model partition coefficients are too low, due to the overestimation of melt peralkalinity in RhyoliteMELTS. We believe that observations of Ba partitioning in the experimental glasses of Henderson and Pirozynski (2012) and the natural unzoned pantelleritic samples of Mahood and Stimać (1990) produce more realistic estimates of partition coefficients (Figure 10).

The natural data from the MER volcanoes show high and variable feldspar rim Ba concentrations (Figure 10a), and melt Ba concentrations of 60 to 850 ppm (Figure 10b), thereby yielding higher and more variable “apparent” feldspar-melt partition coefficients, calculated using feldspar rim values and average melt compositions, than predicted. This is particularly notable in samples from eruptions associated with caldera-forming events (Figures 10c and 10d). Mahood and Stimać (1990) produced *observed* partition coefficients for five pantellerites and trachytes from Pantelleria by averaging data from unzoned phenocrysts, the upper and lower values of the range they calculated are shown in Figures 10c and 10d. The majority of “apparent” partition coefficients calculated for the MER volcanic samples fall within this range, and therefore so do the averaged observed partition coefficient for each sample. However, the spread of “apparent” coefficients is large, producing large standard deviations, particularly for the caldera-forming samples, which show a  $\sigma$  of up to 5.5 (Table 3). Mahood and Stimać (1990) cite zoning as the likely cause of variability in literature values for feldspar-melt Ba partition coefficients; however, this has been ruled out in this study by only using rims of crystals that appear themselves to be unzoned (Figures 7a and 7b). It should also be noted that the data do not show a fall in the partition coefficients, predicted for increasingly evolved (Figure 10c), increasingly peralkaline melts (Figure 10d; Henderson & Pirozynski, 2012; Mahood & Stimać, 1990). However, these studies were limited to rhyolites with <70 wt%  $\text{SiO}_2$  and may not be representative of the high silica rhyolites we present.

We interpret these data (shown in Figures 9 and 10) to show that a portion of the Ba-rich feldspars, particularly within the caldera-forming ignimbrite deposits, are antecrysts, crystallized from a Ba-rich (more primitive) melt, before being entrained into a Ba-depleted (more evolved) melt. One interpretation of this observation is that these antecrysts, during the process of fractional crystallization, were segregated from the melt and stored in a distinct region of the magma reservoir. This crystallization and segregation of alkali feldspars would continually strip the melt of compatible elements, such as Ba, sequestering them in the crystals. At some point before or during eruption, the melt entrained these crystals, which may have been disaggregated from a crystal-rich region of the reservoir. Textural evidence of mush disaggregation can be observed in the prevalence of glomerocrystic clots of feldspars in the crystal-rich ignimbrites. We propose a conceptual structure for the peralkaline magma reservoirs beneath Aluto and Kone that is consistent with the evidence we present here (Figure 11). The reservoir may contain feldspar-rich “mush” regions, with segregated residual liquids in the upper portions. This structure is consistent with the hypothesis that the Daly Gap may be caused by density filtering, with less evolved magmas locked away in crystal-rich mushes (see section 5.2). Postcaldera eruptions primarily tap the residual liquids, with relatively low fractions of antecrysts, while more explosive, larger volume eruptions, associated with caldera-forming events, may excavate a mush pile, erupting a cargo of more Ba-enriched crystals out of equilibrium with the carrier liquid (Figures 9 and 10a). The absence of notable trace element zoning in the antecrysts (Figures 7a and 7b) suggests that conditions are not suitable for rim growth and/or the timescale between crystal accumulation and eruption is short. Ba is a slow diffusing element (Cherniak, 2002), which would require the timescales for equilibration to be long: equilibration of 100- $\mu\text{m}$ -thick rims at 700 °C would require timescales of Ma (Cherniak, 2002). It may be that long-term storage in a “mush region” has resulted in the diffusive homogenization of the crystals, removing any zoning



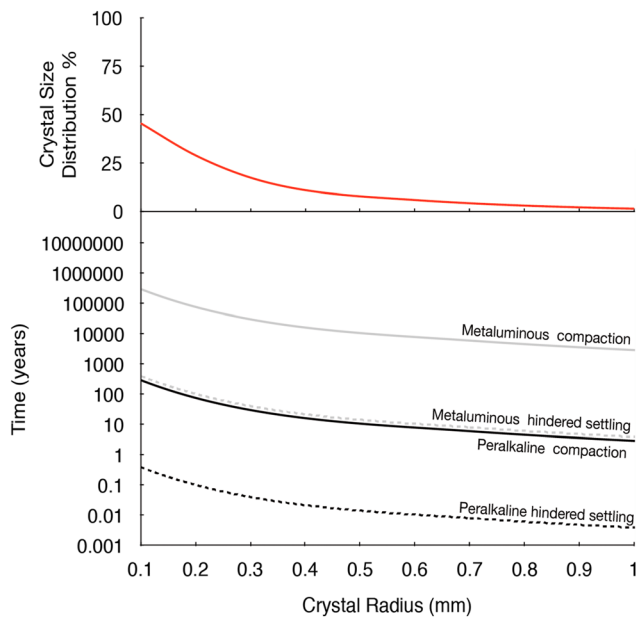
**Figure 11.** Schematic showing the hypothesized structure of peralkaline magma reservoirs beneath Main Ethiopian Rift volcanoes. Peralkaline magmas are fed by a mafic melts that undergo protracted fractional crystallization. The shallow reservoir is dominated by a feldspar-rich mush, built up by crystal-melt segregation, aided by the low-viscosity of peralkaline melts. Feldspar crystallization steadily strips the residual melts of compatible trace elements, such as Ba, leading to a compositional stratification of the mush pile. During explosive caldera-forming eruptions crystals are scavenged from deep in this mush pile, leading to the incorporation of feldspar crystals that are too Ba-enriched to be in equilibrium with their carrier melts. Postcaldera eruptions primarily tap residual melt lenses and do not appear to incorporate significant portions of crystal mush.

developed during growth in a continually evolving liquid, prior to incorporation into their final carrier liquid. We speculate that this crystal scavenging may have taken place during eruption, although the timing of it remains unconstrained.

High crystallinity mush bodies have been inferred to exist in the crust beneath other volcanoes in the EAR. Rooney, Hart, et al. (2012) invoked a crystal-mush model to explain the chemical heterogeneity of the crystal cargo at Chefe Donsa. Macdonald et al. (2008) observed cumulate feldspar-rich xenoliths enriched in Ba, Sr and Eu at peralkaline centers in the Kenyan Rift, while the elevated Ba contents of some melts from the Olkaria Volcanic Complex, Kenyan Rift, have been linked to resorption of remobilised alkali feldspars (Macdonald et al., 2012). Marshall et al. (2009) also observed disequilibrium features in phenocrysts that were tentatively linked to crystal scavenging at Olkaria. At Menengai volcano, there is isotopic consistency between phenocrysts that are out of equilibrium with their carrier melts in terms of trace elements, indicating a common genetic source for the antecrysts (Macdonald et al., 1994). Gibson (1974) also suggested that the differing geochemistry of precaldere and postcaldere deposits at Fentale volcano may even relate to the loss of “fugitive material” during large caldera eruptions. The data from this study supports this link, with lower Ba concentrations observed in the Fentale postcaldere whole-rock, glass and feldspar analyses. The absence of this pattern at Kone may be related to the volcanoes history of multiple caldera eruptions, where pre-Kone caldera samples may also be viewed as post-Birenti caldera samples. The only noncaldera sample to contain feldspars with significant Ba concentrations was the singular pre-Birenti obsidian investigated.

#### 5.4. Timescales of Crystal Settling and Compaction in a Peralkaline Magma Reservoir

Segregation of liquids and crystals during protracted fractional crystallization is an important process in the evolution of Aluto, Kone, and Fentale peralkaline magmas. Our data suggest that residual melts are stripped of compatible trace elements, such as Ba, which are sequestered in feldspars in crystal mush piles (Figure 11). Observations of crystal-poor peralkaline rhyolites erupted between caldera-forming events requires the



**Figure 12.** Plot showing the time required to segregate  $0.01 \text{ km}^3$  of crystal-poor pantellerite (black lines) and metaluminous rhyolite (gray lines) from crystals by compaction (solid lines) and hindered settling (dashed lines) as a function of the grain size. An example crystal size distribution for a typical Aluto pantellerite postcaldera lava is shown above.

segregation of liquids from crystals on timescales at least reflecting the intereruption periods. The efficiency of settling and compaction may be aided by the relatively low viscosity of peralkaline melts: at  $800^\circ\text{C}$  the Cuddia di Mida pantellerite viscosity lies between  $5 \times 10^3$  and  $5 \times 10^4 \text{ Pa s}$  for  $\text{H}_2\text{O}$  concentrations of 2.5–4.9 wt% (Neave et al., 2012). This low melt viscosity promotes magma differentiation and stratification through crystal settling; Stokes settling velocities of 10, 190, and  $230 \text{ Ma}^{-1}$  were reported for 1 mm grains of plagioclase, augite, and olivine (Neave et al., 2012).

Here we calculate the timescales necessary for melt segregation in a peralkaline system similar to Aluto following the method of Bachmann and Bergantz (2004; for details of the modeling see supporting information S4–S6; Barnea & Mizrahi, 1973; Davis & Scrivos, 1985; Jackson et al., 2003; McKenzie, 1984; Rabinowicz et al., 2001; Shirley, 1986). A melt viscosity of  $10^2 \text{ Pa s}$  was used for the peralkaline melt, based on the model of di Genova et al. (2013) for a melt with 5 wt. %  $\text{H}_2\text{O}$  and a temperature of  $765^\circ\text{C}$ , values which are considered representative for MER volcanics (Gleeson et al., 2017; Webster et al., 1993). We assume a density contrast between melt and crystals of  $170 \text{ kg/m}^3$ , based on the dominance of alkali feldspar ( $2550\text{--}2630 \text{ kg/m}^3$ ) and quartz ( $2650 \text{ kg/m}^3$ ), and a melt density of  $2390 \text{ kg/m}^3$  (following Bottinga & Weill, 1970). All particles are assumed to be spherical, and therefore, these timescales are minima owing to the decrease in settling velocity within a fluid with departure of a grain from a spherical shape (Komar & Reimers, 1978).

Porosity was set at 50% for compaction calculations based on estimates of when a rigid crystal framework is formed for spherical particles (Vigneresse et al., 1996); crystal fraction was set at 10% for hindered settling calculations based on the upper end of phenocryst contents in postcaldera eruption deposits; see supporting information S7 and S8 for the effect of varying these parameters. Magma reservoir geometries were calculated assuming an elliptical cylinder. The elliptical cross section had a long axis of 8 km and short axis of 5 km, in line with the estimate of caldera size by Hutchison et al. (2015). There is considerable uncertainty on the estimate of reservoir size. If the elliptical cross section used has 50% less area then all estimates of compaction timescales will be an order of magnitude faster, while all estimates of hindered settling will be two times slower (see supporting information S9). The model setup is shown in supporting information S5. Timescales of melt segregation for a metaluminous rhyolite melt were modeled for comparison. Melt viscosity in this case was assumed to be  $10^5 \text{ Pa s}$ , assuming a similar melt temperature and water content (Scaillet et al., 1998).

Mean eruption intervals at Aluto have been estimated at 300–400 years for postcaldera pantellerites (Figure 12; Fontijn et al., 2018). We calculated the timescales required to segregate  $0.01 \text{ km}^3$  and  $1 \text{ km}^3$  of melt, consistent with the range in eruptive volumes of crystal-poor postcaldera eruptions at Aluto. For a mean grain size of 0.2 mm, it would take on the order of months to tens of years to segregate  $0.01\text{-km}^3$  melt (Figure 12), and tens of years to ten thousands of years to segregate  $1\text{-km}^3$  melt from a crystalline mush, if we treat the magma reservoir as one coherent body. The eruption intervals are typically greater than the upper limits required for melt segregation suggested by the calculations, implying that there is sufficient time between eruptions to extract enough melt for a postcaldera eruption of crystal-poor magma. It must be stressed that this is a simple model; it may be that there are multiple regions of melt accumulation in the reservoir, which would then decouple the eruption frequency from the time scale needed to accumulate a particular volume of melt. Our results do highlight, however, that crystal-melt segregation is faster for peralkaline systems, with more than an order of magnitude difference between the timescales versus a metaluminous system (Figure 12).

### 5.5. Pre-Eruptive Magma Storage Conditions

The pre-eruptive melt temperature of the Kone basaltic scoria was estimated using the clinopyroxene-liquid thermobarometer of Neave and Putirka (2017; see supporting information 10 and 11 for further

details). Clinopyroxene-melt equilibrium was last achieved at a temperature of  $1150\text{--}1170 \pm 60$  °C and pressures of  $420\text{--}575 \pm 140$  MPa, equivalent to a depth of  $15\text{--}21 \pm 5$  km assuming an average crustal density of  $2,800 \text{ gm}^{-3}$  (Wilks et al., 2017). The Fe-Mg partitioning relationship between clinopyroxene and melt was used to select appropriate crystal rims for analysis. Observed partition coefficients ( $D_{\text{Fe-Mg}}$ ) between the pyroxenes melt all lay within error of the 0.27 equilibrium value (Putirka, 2008).

The pre-eruptive temperature of the pantellerites at Aluto was estimated by Gleeson et al. (2017) at  $718\text{--}765 \pm 23$  °C using an alkali feldspar thermometer (Putirka, 2008) and assuming an equilibration pressure of 150 MPa based on estimates using RhyoliteMELTS models (Gualda et al., 2012). These pressures convert to depths of  $5.4 \pm 1$  km assuming an average crustal density of  $2,800 \text{ gm}^{-3}$  (Wilks et al., 2017). Experimental studies have shown that the phase assemblage of alkali feldspar, clinopyroxene, aenigmatite, and ilmenite is stable at 1.0–1.5 kbar at near  $\text{H}_2\text{O}$ -saturated conditions and temperatures of  $680\text{--}725$  °C (di Carlo et al., 2010), largely consistent with the Aluto observations. Further north, in the Afar region, Field et al. (2012) analyzed melt inclusions from the peralkaline Dabbahu volcano, finding volatile saturation pressures in the range of 43–207 MPa, also consistent with shallow magma storage, at  $\sim 1\text{--}5$  km depth in the crust.

However, it should be noted, concerning temperature estimates, that we have highlighted complex crystal cargoes in pantellerite samples at Aluto, containing numerous alkali feldspars that are likely to be out of equilibrium with their host melts. These can often be difficult to identify based on petrographic observations and major element analysis alone. If temperatures are higher than estimated by Gleeson et al. (2017), calculated feldspar-melt Ba partition coefficients will be lower, and thus predicted melt Ba based on feldspar rim compositions will be higher. If lower than estimated, partition coefficients will be higher and predicted melt Ba contents lower.

## 6. Implications of our Study for Geophysical Imaging of Peralkaline Magma Reservoirs

While whole-rock and glass compositions of erupted products from Aluto, Kone, and Fentale reflect prolonged fractional crystallization (Figures 3–5), trace element heterogeneity in the crystal cargoes (Figures 9 and 10a) is indicative of more complex processing including mixing and crystal scavenging, perhaps from a mush-dominated magma storage system. In support of a mush-dominated system, low-viscosity peralkaline liquids allow for efficient crystal-melt segregation (Figure 12) building mush piles where intermediate composition melts are locked away, and compatible elements, such as Ba, are sequestered. We suggest that crystal-rich ignimbrites, associated with caldera-forming events, may be able to scavenge Ba-enriched antecrysts from this region (Figure 11). Postcaldera eruptions primarily tap residual melt, segregated in small melt lenses in the upper portions of the reservoir, with a much lower fraction of scavenged antecrysts.

Magnetotelluric surveys, used for inferring the Earth's subsurface electrical conductivity, have been conducted at several sites along the EARS (Desissa et al., 2013; Hübert et al., 2018; Johnson et al., 2015; Samrock et al., 2015; Whaler & Hautot, 2006). Resistivity is sensitive to fluid content, allowing the method to identify the presence of partial melt beneath volcanoes (Desissa et al., 2013; Johnson et al., 2015). However, the electrical conductivity of magmatic reservoirs is dependent on the state of the magma itself, in terms of melt volatile abundance, temperature, composition, and crystal content (Gaillard & Iacono Marziano, 2005). The electrical conductivity of silicate liquids varies within a range of  $10^{-2}\text{--}10^1 \text{ } \Omega/\text{m}$  (Gaillard, 2004; Tyburczy & Waff, 1985; Waff & Weill, 1975), while the conductivity of crystals can be in the range of  $10^{-10}\text{--}10^{-3} \text{ } \Omega/\text{m}$  (Huebner & Dillenburg, 1995), making them insulators. A highly crystalline mush, with a low melt fraction, may appear as a resistive structure (Hübert et al., 2018). Indeed, despite the petrological estimates for shallow magma storage at Aluto (Gleeson et al., 2017), as described above, magnetotelluric methods have not identified an area of increased electrical conductivity in the crust (Hübert et al., 2018; Samrock et al., 2015) that might indicate the presence of partial melt (e.g., Hoffman-Rothe et al., 2001; Pous et al., 1999; Schilling & Partzsch, 2001). At shallow depths a conductive clay cap to the hydrothermal system is proposed, while at greater depths the crust appears increasingly resistive (Hübert et al., 2018; Samrock et al., 2015).

Small lenses of residual melt in the upper part of the system, which we hypothesize feed the crystal-poor postcaldera eruptions, accumulate over short timescales ( $10^{-1}\text{--}10^1$  years). Small-volume liquid lenses may



be difficult to capture and resolve using conductivity surveys due to the inherently low spatial resolution of the technique. The ephemeral nature of these liquid lenses poses new challenges when imaging and monitoring peralkaline magmatic-volcanic systems, with a need to better understand the limits of detection and the time-dependent evolution of magmatic storage regions. The presence of a conductive anomaly at Boset-Bericha volcano (Whaler & Hautot, 2006), for example, may reflect the time-sensitive capture of a short-lived melt lens, although it could also indicate the presence of a longer-lived more melt-rich, interconnected system. The scenarios at both Aluto and Boset-Bericha are in stark contrast to electrical resistivity surveys carried out further north in the Afar region. Here large regions of low resistivity have been imaged reaching down to 35 km depth, interpreted as long-lived reservoirs containing ~13% melt fraction and extending down into the mantle (Desissa et al., 2013).

Other geophysical data from Aluto are consistent with a magma reservoir system extending to depths of 9 km and deeper. A local network of 12 seismometers was deployed at Aluto between 2012 and 2014, detecting more than 2,000 earthquakes in a 24-month period (Wilks et al., 2017). A shallow zone (at 0–2 km) of high seismicity and high *b* values (a parameter describing the relative abundance of large to small magnitude events) likely corresponds to the active hydrothermal system, while deeper events (2–9 km) reflect high strain rates where magmatic fluids cause elastic deformation (Wilks et al., 2017). At depths greater than 9 km the crust appears largely aseismic, interpreted as an area of underlying ductile magmatic mush (Wilks et al., 2017). These interpretations are largely consistent with those arising from InSAR observations of deformation at Aluto. A period of inflation in 2008 is best explained by a deformation source at  $\sim 5.1 \pm 0.5$  km depth, thought to reflect fluid injection into the roof zone of a magma storage region (Hutchison, Biggs, et al., 2016). A subsequent period of long-term subsidence was interpreted as magmatic degassing and depressurization of the hydrothermal system (Hutchison, Biggs, et al., 2016). Mahatsente et al. (1999) additionally located a positive gravity anomaly within the shallow crust beneath Aluto during a regional survey. This could be consistent with the presence of crystalline magmatic intrusions, and may provide evidence for density filtering of intermediate magmas forming a Daly Gap at Aluto (see section 5.2). Mattia et al. (2007) suggested that trapped high-density intermediate magmas at Pantelleria may contribute to the positive gravity anomalies observed there.

InSAR observations of the Afar region have also been used to suggest shallow magmatic storage beneath volcanoes such as Dabbahu (Field et al., 2012; Grandin et al., 2010; Wright et al., 2006). Here a broad area of uplift, ~20 km in diameter, was shown to be consistent with a modeled scenario of stacked sills at 1- to 6 km depth. Seismic data obtained during the same period of unrest indicated similar depths of storage (Ayele et al., 2007; Ebinger et al., 2008; Field et al., 2012). While silicic centers in the Afar region, such as Dabbahu, may appear similar to those of the MER in terms of peralkaline compositions and shallow storage, contrasting crustal electrical resistivity again highlights key differences. In this more mature Afar rift, large volumes of partial melt are stored throughout the crust (Desissa et al., 2013), magma flux to the surface appears to be greater (Hutchison et al., 2018) and eruptions are more frequent. At least five eruptions have occurred in Afar during the period of modern remote sensing (e.g., Allard et al., 1979; Ayele et al., 2007, 2009; Ferguson et al., 2010; Grandin et al., 2010; Wright et al., 2006; Yirgu et al., 2006), whereas none have occurred in the MER. Silicic magmatic plumbing in the Afar region is also clearly linked to the rifting cycle. For example, Wright et al. (2006) showed that much of the melt supplied to a major dyking episode in 2005 was sourced from shallow chambers beneath the Dabbahu and Gabho volcanoes. In Afar magma storage reservoirs appear to be more connected and, potentially, laterally extensive (Biggs et al., 2016; Ebmeier et al., 2018; Xu et al., 2017) compared to the MER, where we hypothesize small portions of melt stored in poorly connected, ephemeral lenses.

## 7. Conclusions

While whole-rock and glass compositions are modeled effectively by fractional crystallization, this simple model cannot explain the trace element (Ba) heterogeneity observed in the crystal cargoes from eruptive products at Aluto, Kone, and Fentale volcanoes. Many of the feldspars, particularly in samples from caldera-forming eruptions, are antecrysts, crystallized from a Ba-enriched (more primitive) melt, before being segregated during the process of fractional crystallization, and later entrained in Ba-depleted (more evolved) residual liquids. We propose that these antecrysts are sourced from a crystal-rich region of the magma

reservoir (perhaps a mush) that is excavated during the largest eruptions, creating crystal-rich trachytes and rhyolites typical of caldera-forming eruptions.

The low-viscosity nature of peralkaline rhyolitic liquids causes crystal-melt segregation to occur on faster timescales than for metaluminous rhyolites (which are more viscous). Separated crystals sequester compatible elements such as Ba, while residual melts continue to evolve, likely going on to feed postcaldera eruptions. The timescales necessary for the segregation of enough residual, eruptible melt to feed a crystal-poor postcaldera eruption ( $0.01\text{--}1\text{ km}^3$ ) are short ( $10^1\text{--}10^4$  years). These isolated melt lenses may be small and ephemeral, perhaps making them difficult to resolve using geophysical techniques (seismic tomography, electrical conductivity). The interpretation that peralkaline systems may spend portions of their life cycle dominated by crystalline mushes helps reconcile contrasting geophysical data for Aluto.

Our study highlights the absence of experimental data for Ba partitioning behavior in silica-rich peralkaline melts; and the deficiencies in the RhyoliteMELTS model at reproducing peralkalinity for the rhyolitic end of the magma series. This causes partitioning models, which depend on peralkalinity, to consistently underestimate feldspar-melt partition coefficients for Ba and feldspar Ba contents. A previous study suggested that Ba feldspar-melt partition coefficients drop steeply with peralkalinity despite accompanying modest increases in  $\text{SiO}_2$  and drop in temperatures (Mahood & Stimpac, 1990); however, this study, and the experimental data of Henderson and Pirozynski (2012), was limited to rhyolites with  $<70\text{ wt\% SiO}_2$ . Petrological experiments on more evolved peralkaline magmas are needed to improve our understanding of Ba partitioning in peralkaline rhyolitic magmas.

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